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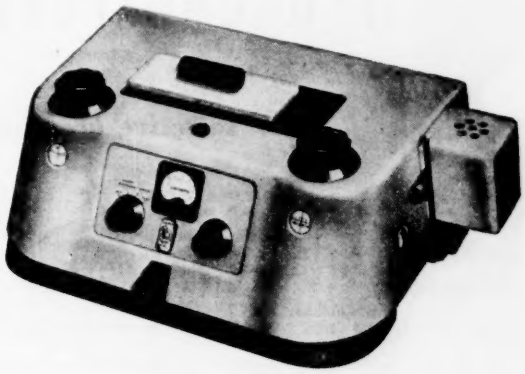

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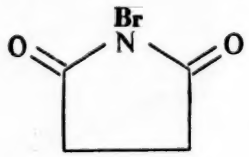

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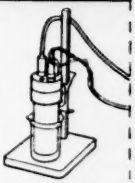

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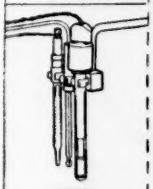

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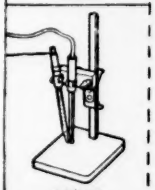

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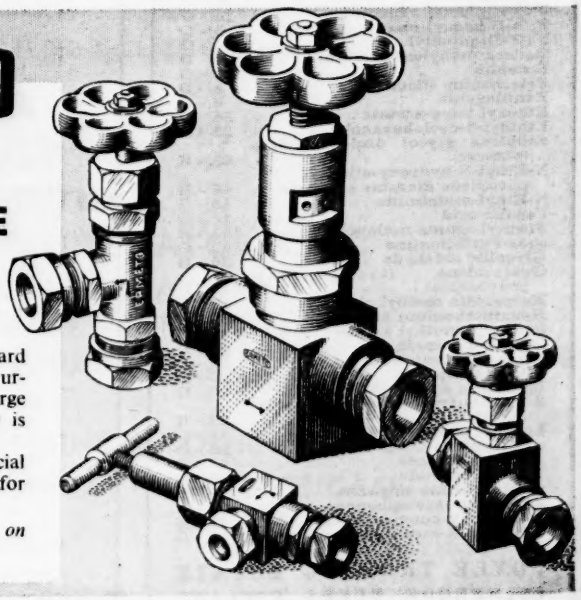

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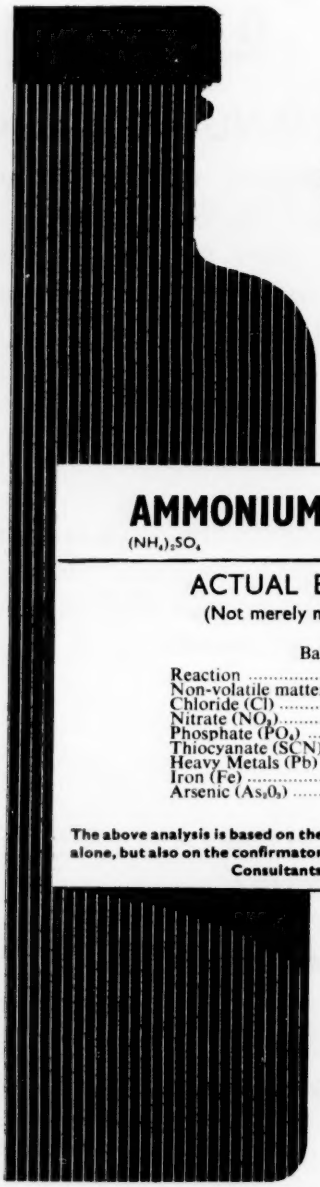

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(Not merely maximum impurity values)

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Reaction	pH	5·2
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Chloride (Cl)		0·00012%
Nitrate (NO_3)		0·00023%
Phosphate (PO_4)		0·00002%
Thiocyanate (SCN)		0·0002%
Heavy Metals (Pb)		0·00005%
Iron (Fe)		0·00002%
Arsenic (As_2O_3)	less than	0·00001%

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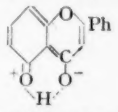
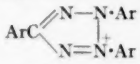
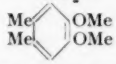
ERRATA.

Vol.	Page.	Line.	
1949	2915	6 *	*For* tetrahedral *read* planar.
1950	1449		Third equation *should read* $$\int_{[A]_0}^{0} d[A] = \int_{[B]_0}^{[B]_\infty} \left(\frac{k_1}{k_2[B]_0} + 1\right) d[B]$$
1951	2107	31	*For* $Ph{\cdot}CO_2H_2^+$ *read* $Ph_3C{\cdot}OH_2^+$.
	2109		Legend to Fig. 8 For *trinitrophenylcarbinol* read *trinitrotriphenylcarbinol*.
	2111		Abscissa of Fig. 9 *For* $2H_0 + log(H_2O)$ *read* $2H_0 + log[H_2O]_{st}$.
	3330	6 *	*For* (Irvin and Irvin, *J. Amer. Chem. Soc.*, 1946, **68**, 2181) *read* (Irvin and Irvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1091).
1952	1364		First Table, values under headings d^{20} and d^{25} *should read*

Ref.	d^{20}	d^{25}
B	0·8071	0·8039
C	0·9035	0·9002
E	0·8820	0·8787

	1531	2 *	*For* 2 : 4 : 5-trichlorophenol *read* 2 : 4 : 5-trichlorophenetole.
	1928	6 *	*For* 0·27 g. *read* 0·54 g.
	3572	11	*For* Professor Jensen *read* Craig *et al.*, quoted by Orgel.
	3791	8	*For* R′ = R″ = H *read* R′ = R″ = Ac.
	4641		Formula (I) *should read* 
	5028		Table 2, second column, penultimate entry *For* 5 : 7-$(OMe)_2$ *read* 5-OMe.
1953	14	19	*For* $C_{13}H_{22}O_3$ requires C, 73·8 *read* $C_{17}H_{24}O_3$ requires 73·9.
	146		Experimental, first line *For* α-Methyl *read* γ-Methyl.
	180	6	*Delete* (7·7 g.).
		7	*For* (6·5 g.) *read* [(i) 7·7 g., (ii) 6·5 g.].
		9 *	*For* 9-azidofluorenyl azide *read* 9-azidofluorene.
	325		Formula (I) *should read* 
	483		Summary, line 4 *For* 9 : 10-benzonaphtho(2′ : 3′-4 : 5)pyrene *read* 8 : 9-benzonaphtho(2′ : 3′-3 : 4)pyrene.
	820		Formula (IV) *should read* 
	857	Last	*For* more polarized *read* pre-polarized.
	893	5 *	*For* benzoxanthen *read* xanthen derivative.
	1101	19	*For* hydrated ferric oxide *read* hydrated ferric phosphate.

* From bottom of main text.

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453. *The Stepwise Hydrogenation of Dimethyl Docosa-10 : 12-diynedioate.*

By J. P. Riley.

Dimethyl docosa-10 : 12-diynedioate has been synthesised by oxidative coupling of the cuprous derivative of methyl undec-10-ynoate. Hydrogenation of the conjugated diacetylenic ester over Raney nickel at 100° yields dimethyl docosa-10-ynedioate and docosa-10-enedioate simultaneously. Before appreciable amounts of the fully saturated ester are formed all the monoyne is converted into monoene. Only an insignificant amount of conjugated diene is formed during the hydrogenation, in contrast with the findings of other workers using other types of diacetylenic compounds. Both the *cis*- and the *trans*-mono-olefins are produced; they have been characterised by oxidation of the corresponding acids to their dihydroxy-compounds.

The seed oil of *Onguekoa Gore* Engler has been claimed (Steger and van Loon, *Rec. Trav. chim.*, 1940, **59**, 1156; Castille, *Annalen*, 1939, **543**, 104) to contain among its component fatty acids a conjugated diacetylenic acid (isanic acid; octadec-17-ene-9 : 11-diynoic acid). During an investigation of this oil it was thought desirable to study the hydrogenation of a typical long-chain conjugated diacetylene, since few such compounds had been investigated. Kuhn and Wallenfels (*Ber.*, 1938, **71**, 1889) and Zal'kind and Gversiteli (*J. Gen. Chem., U.S.S.R.*, 1939, **9**, 971) showed that hydrogenation of diacetylenic glycols $(OH{\cdot}CRR'{\cdot}C{\equiv}C{\cdot})_2$ over palladium yielded the corresponding diethylenic glycol, but over platinum or nickel only the fully saturated glycols. Ott and Schroter (*Ber.*, 1927, **60**, 624) hydrogenated diphenyldiacetylene over nickel in ether and obtained solely *cis-cis*-diphenylbutadiene; use of palladium resulted in a mixture of diphenylbutadienes (*cis-trans* 68%; *cis-cis* 25%; *trans-trans* 0·17%). Lauer and Gensler (*J. Amer. Chem. Soc.*, 1945, **67**, 1171) found that dodeca-2 : 10-diynedioic acid was smoothly hydrogenated at room temperature in the presence of Raney nickel to dodecanedioic acid.

For the present investigation dimethyl docosa-10 : 12-diynedioate was synthesised by oxidative coupling of methyl undecynoate (cf. Bowden, Heilbron, Jones, and Sergeant, *J.*, 1947, 1579), and its identity proved by a molecular-weight determination and oxidation to sebacic acid. The ester, which was a stable colourless solid, showed the characteristic ultra-violet absorption bands of low-intensity (cf. Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 2003). The corresponding acid and its *p*-bromophenacyl ester were rapidly but partly converted into pink and blue polymers respectively (cf. Armitage *et al.*, *loc. cit.*).

The pure diacetylenic ester with a 7·5% solution of potassium hydroxide in ethylene glycol at 180° (60 minutes; cf. Hilditch, Morton, and Riley, *Analyst*, 1945, **70**, 67) was converted into a substance showing absorption at 283 and 235 mμ ($E^{1\%}_{1\,cm.}$ 87·0 and 92·0 respectively).

The diacetylenic ester was hydrogenated at 100° by using Raney nickel since these are the conditions usually employed for fatty acid derivatives. Fractions withdrawn during the reaction were analysed as follows: (i) Unchanged diacetylenic compound was estimated by alkali-isomerisation followed by spectrophotometry at 283 mμ. (ii) Conjugated diene was determined from the absorption of the fraction at 232 mμ after deduction of the absorption due to the unchanged diacetylene. (iii) Fully saturated ester was determined by acetone–permanganate oxidation followed by removal of acidic oxidation products. (iv) Monoacetylenic ester and monoethenoid ester were determined from the amount of hydrogen absorbed, after allowance had been made for the other products. Compounds containing diene or enyne unsaturation show strong selective absorption in the region 226—232 mμ ($\varepsilon_{max.}$ *ca.* 28,000 and 15,000 respectively). When absorption due to unchanged diyne is taken into account it is seen (Fig. 1) that the total amount of unsaturation of this type in each fraction never exceeds 5% and in fractions 1—3 is less than 3%. For calcul-

ations all absorption in this region has been assumed to arise from a conjugated diene, though there is probably a mixture of diene and enyne.

These analyses, shown in Fig. 2, indicated that the initial product of the hydrogenation was dimethyl docosa-10-ynedioate (II), formed by the addition of two molecules of hydrogen. After approximately 25% of the theoretical amount of hydrogen had been absorbed (*i.e.*, 1 mol.), formation of the ethylenic compound (III) set in at the expense of both the di-

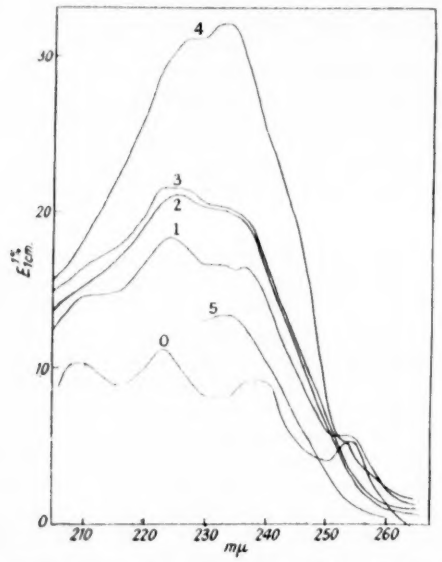

FIG. 1.
Absorption spectra of fractions.

and the mono-acetylenic compound, increasing to a maximum of 83% at 75% hydrogenation. Beyond this stage the fully saturated dimethyl docosanedioate (IV), which had hitherto been produced in very small amounts, was formed by addition of hydrogen to (III).

$$\underset{\text{(I)}}{MeO_2C\cdot[CH_2]_8\cdot C{:}C\cdot C{:}C\cdot[CH_2]_8\cdot CO_2Me} \xrightarrow{2H_2} \underset{\text{(II)}}{MeO_2C\cdot[CH_2]_8\cdot C{:}C\cdot[CH_2]_{10}\cdot CO_2Me} \xrightarrow{H_2}$$

$$\underset{\text{(III)}}{MeO_2C\cdot[CH_2]_8\cdot CH{:}CH\cdot[CH_2]_{10}\cdot CO_2Me} \xrightarrow{H_2} \underset{\text{(IV)}}{MeO_2C\cdot[CH_2]_{20}\cdot CO_2Me}$$

To determine whether the monoacetylene had been formed by Thiele addition of 2 molecules of hydrogen and triple bond shift (which would yield $MeO_2C\cdot[CH_2]_9\cdot C{:}C\cdot[CH_2]_9\cdot CO_2Me$), a 50% hydrogenated fraction was oxidised with potassium permanganate in acetone; the only dibasic acids recovered were sebacic and dodecanedioic acids, showing that triple-bond shift had not occurred.

Attempts were made to identify the monoacetylenic compound by iodination but the resultant di-iodo-compound was too unstable for analysis.

After absorption of 78% of the theoretical amount of hydrogen the product was fractionally crystallised from acetone at low temperatures; it yielded approximately equal amounts of the *cis*- and the *trans*-form of dimethyl docosa-10-enedioate (III), which were characterised by hydrolysis and oxidation to the corresponding dihydroxy-acids. The position of the double bond in both isomers was confirmed by oxidation. The infra-red absorption spectra of the isomers were practically identical, owing perhaps to the fact that the compounds are almost symmetrical, symmetrical vibrations not being infra-red active.

The formation of both a *cis*- and a *trans*-ethylene by hydrogenation of an acetylene is very unusual, since the normal product is only the *cis*-isomer. Thus Gonzalez (*Anal. Fis. Quím.*, 1926, **24**, 156), using a nickel catalyst, obtained oleic and erucic acid (both *cis*)

by hydrogenation of stearolic and behenolic acid respectively. These observations have been confirmed and extended to other types of compounds by many later workers. The method has been frequently employed for the synthesis of the naturally occurring (*cis*-)-isomers of fatty acids. Adkins and Billica (*J. Amer. Chem. Soc.*, 1948, **70**, 695) on the other hand claimed to have hydrogenated stearolic acid to elaidic acid (identified by melting point only), by using W6 Raney nickel. Ott (*Ber.*, 1928, **61**, 2119) found that in the presence of highly active catalysts, such as platinum black, only *cis*-isomers were formed, but with less active or poisoned catalysts variable amounts of the *trans*-isomer were also produced.

In the present work, the monoethenoid ester could have arisen either by direct addition of 3 mols. of hydrogen to the diacetylene, or by addition of 1 mol. to the previously formed monoacetylenic compound (II). The latter reaction would probably give solely the *cis*-isomer; the former on the other hand might yield the equilibrium mixture of *cis*- and *trans*-forms. The rate of hydrogenation revealed no discontinuity until only saturated and monoethenoid compounds were present.

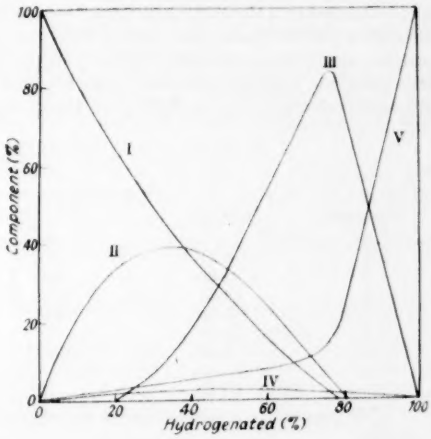

FIG. 2. *Composition of hydrogenated fractions.*
I. Dimethyl docosa-9 : 11-diynedioate.
II. Dimethyl docosa-9-ynedioate.
III. Dimethyl docos-9-enedioate.
IV. Dimethyl docosa-9 : 11-dienedioate.
V. Dimethyl docosanedioate.

Earlier studies of the hydrogenation of conjugated diacetylenic compounds have yielded as first product the conjugated diene, but the compounds investigated contained another functional group (hydroxyl or phenyl) adjacent to the triple bonds which might have affected the course of reaction.

EXPERIMENTAL

Preparation of Dimethyl Docosa-10 : 12-diynedioate.—10 : 11-Dibromoundecanoic acid (450 g.) was dehydrobrominated with aqueous potassium hydroxide (62%) at 150° for 8 hr. The liberated crude undecynoic acid (360 g.) was esterified at room temperature with methyl alcohol containing 1% of concentrated sulphuric acid. The resultant ester, fractionated *in vacuo* to separate it from hydroxylated and polymerised products, gave methyl undec-10-ynoate (289 g.), b. p. 90°/1 mm., n_D^{15} 1·4506 [Found: I.V. (Wijs), 155·5; I.V. (Toms), 248·1. Calc. for $C_{12}H_{20}O_2$: I.V., 249·0].

Methyl undec-10-ynoate (120 g.) in ethyl alcohol (800 ml.) was added dropwise with constant stirring to a solution of cuprous chloride (160 g.), ammonium chloride (280 g.), and hydrochloric acid (8 ml.) in water (1200 ml.). The mixture was heated to 55° and a current of air passed through it until the yellow-green precipitate of the cuprous derivative of the acetylenic ester had almost disappeared (2½ hr.). The cold mixture was poured into water and extracted with ether. The ethereal layer was washed several times with water and filtered to remove copper salts. The crude diacetylenic ester (116 g.), recovered by evaporation, was crystallised first from ether (10 ml./g.) at −70°, and then from ether (30 ml./g.) at −50°. The yield of pure dimethyl docosadiynedioate, m. p. 42·5°, was 92·5 g. [Found: C, 74·1; H, 9·8%; I.V. (Wijs, 0·1 g., 30 min.), 121·0; I.V. (Toms), 132·7; I.V. (hydrogenation), 260·0; sap. equiv., 194·7; *M* (Rast), 383·5. Calc. for $C_{24}H_{38}O_4$: C, 73·8; H, 9·8%; I.V., 260·3; sap. equiv.,

195·2; *M*, 390·5]. Absorption max. (in EtOH): 210, 223, 239, and 254 mμ (ε 400, 435, 366, and 216 respectively). After the ester had been heated with 7·5% potassium hydroxide in ethylene glycol at 180° for 60 min. (Hilditch *et al.*, *loc. cit.*), absorption maxima appeared at 235 and 283 mμ ($E^{1\%}_{1\,cm.}$ 92·0 and 87·0 respectively).

The ester (1·04 g.) was oxidised with potassium permanganate (8 g.) in acetone (20 ml.). Hydrolysis then gave 0·43 g. of sebacic acid, m. p. (from water) and mixed m. p. 130—131°.

The dimethyl ester was hydrolysed with alcoholic potassium hydroxide. The recovered acid, recrystallised from alcohol, was a white powder, m. p. 114—115°, which soon became covered with an insoluble pink polymer (Found: C, 72·7; H, 9·1. Calc. for $C_{22}H_{34}O_4$: C, 72·8; H, 9·4%).

The potassium salt of the acid was refluxed with an excess of an aqueous-alcoholic *p*-bromophenacyl bromide. The resultant *p*-bromophenacyl ester formed colourless plates, m. p. 103—104° (from alcohol), which rapidly became blue (Found: Br, 21·1. Calc. for $C_{38}H_{44}O_6Br_2$: Br, 20·9%).

Hydrogenation.—The dimethyl ester (59 g.) was hydrogenated at 100° in the presence of *ca.* 1 g. of Raney nickel (Pavlic and Adkins, *J., Amer. Chem. Soc.*, 1946, **68**, 1471). The apparatus consisted of a three-necked flask fitted with a mechanical stirrer (*ca.* 1300 r.p.m.) operating through a packed gland, and with a tube reaching to the bottom of the flask, by means of which samples could be withdrawn without stopping the hydrogenation. Fractionation of the product gave the results shown in Table 1. The results of permanganat oxidatione (Table 2) and of analysis discussed on p. 2193 gave the compositions shown in Table 3.

TABLE 1.

Fraction	Wt. (g.)	Hydrogenated * (%)	I.V.†	$E^{1\%}_{1\,cm}$ at (mμ) 232	254	283 ‡
0	—	0	121	8·33	5·54	87·0
1	5·11	20	106·7	16·70	5·80	53·7
2	5·60	40	102·2	20·33	5·00	33·5
3	13·87	50	80·9	20·41	3·71	22·9
4	3·00	65	70·1	32·20	3·65	7·9
5	23·05	78	56·7	13·20	3·20	—
6	8·00	100	0·6	—	—	—
	Total 58·63					

* Expressed as a percentage of the volume of hydrogen required for complete saturation (*i.e.*, 4 mols.).
† I.V. (Wijs), sample wt. 0·1 g., reaction time 30 min.
‡ After alkali-isomerisation at 180° for 60 min.

TABLE 2.

Fraction	Wt. oxidised (g.)	Wt. of dibasic acid recovered (g.)	Wt. of unoxidised material (g.)	I.V. of unoxidised material	Saturated material (%)
0	1·04	0·43	0·01	—	—
1	4·22	—	0·147	13·6	3·0
2	3·83	2·71	0·221	11·1	5·1
3	13·13	10·25	0·961	5·8	6·8
4	1·74	1·18	0·155	9·4	7·7
5	15·74	—	2·55	2·0	15·6

TABLE 3. *Percentage composition of fractions.*

Fraction	Hydrogenated (%)	Saturated	Monoene	Monoyne	Conj. diene	Conj. diyne
0	0	0	0	0	0	100
1	20	2·9	0	33·9	1·5	61·7
2	40	5·2	18·1	38·5	2·0	38·5
3	50	6·8	37·9	26·9	2·1	26·3
4	65	7·7	61·5	18·0	3·7	9·1
5	78	14·3	82·3	1·9	1·5	—
6	100	100·0	0	0	0	0

***Further Examination of Fractions.—Fraction* 3.** (i) Oxidation. The dimethyl esters of the dibasic acids from the acetone–permanganate oxidation of fraction 3 (see Table 2) were fractionated under reduced pressure through a micro-fractionation column, with results shown in Table 4.

Fraction 3.1. The acids obtained by hydrolysis had m. p. 84—98°, raised to 97—98° by

crystallisation [mixed m. p. with azelaic acid (m. p. 103°), 92—93°]. They probably consisted of sebacic acid contaminated with small amounts of lower dicarboxylic acids which are always formed during acetone–permanganate oxidations.

TABLE 4.

Fraction	Wt. (g.)	B. p./*ca.* 1 mm.	Sap. equiv.	Fraction	Wt. (g.)	B. p./*ca.* 1 mm.	Sap. equiv.
3.1	1·765	—90°	105·9	3.5	1·109	108°	118·1
3.2	1·227	90—96	110·0	3.6	1·093	116	122·0
3.3	1·203	96—103	116·4	3.7	1·579	117 *	124·0
3.4	1·140	103	115·2	3.8	0·376	Residue	143·6

* Falling.

Fractions 3.3 and 3.4. The combined acids (1·79 g.) from these fractions were crystallised twice from water, and twice from ethyl acetate, yielding 0·46 g. of sebacic acid, m. p. and mixed m. p. 128—130°. The soluble material recovered from the second crystallisation from water, on recrystallisation, yielded 0·03 g. of acids, m. p. 106—108° [mixed m. p. with undecanedioic acid (m. p. 109°), 93°].

Fraction 3.5. The acids (0·398 g.) yielded on crystallisation 0·080 g. of sebacic acid and 0·130 g. of acids, m. p. 100—107°, not identical with undecanedioic acid.

Fraction 3.6. The recovered acids (0·92 g.) were boiled with water and the insoluble acids (0·15 g.) recrystallised from ethyl acetate at 0°, yielding dodecanedioic acid (0·12 g.), m. p. and mixed m. p. 128°. A small fraction of m. p. 107—108°, not identical with undecanedioic acid, was obtained by repeated crystallisation of the acids soluble in boiling water.

(ii) Iodination. The acids from fraction 3 were iodinated as described by James and Sudborough (*J.*, 1907, **91**, 104); the di-iodo-compound which was obtained as pale yellow plates partly decomposed before analysis (Found : I, 36·5%. Calc. for $C_{22}H_{38}O_4I_2$: I, 40·9%).

Fraction 5. This was crystallised from acetone at low temperatures, with results shown below :

Fraction	Wt. (g.)	I.V.	Soluble in $COMe_2$	Insoluble in $COMe_2$
S_1	6·02	39·5	—	10 pts. at 0°
L_2	1·64	57·5	10 pts. at 0°	15 ,, −30°
L_3	2·20	64·7	15 ,, −30°	10 ,, −30°
L_4	2·70	64·1	10 ,, −20°	10 ,, −30°
L_5	1·68	64·1	12 ,, −20°	10 ,, −20°
S_5	6·57	64·6	—	12 ,, −20°

Fraction S_5 was dimethyl *trans*-docos-10-enedioate, m. p. 31—32°, n_D^{40} 1·4523 (Found : sap. equiv., 197·6; I.V., 64·6. Calc. for $C_{24}H_{44}O_4$: sap. equiv., 198·2; I.V., 64·5).

Fraction L_3 was substantially pure dimethyl *cis*-docos-10-enedioate, n_D^{40} 1·4523 (Found : C, 72·7; H, 11·0%; sap. equiv., 200·0; I.V., 64·7. Calc. for $C_{24}H_{44}O_4$: C, 72·6; H, 11·2%; sap. equiv., 198·2; I.V., 64·5).

The unsaturated dicarboxylic acids obtained by hydrolysis of fractions L_3 and S_5 were oxidised to the corresponding dihydroxy-acids by dilute aqueous permanganate (cf. Lapworth and Mottram, *J.*, 1925, **127**, 1628); results are :

	cis.	*trans*.
M. p. of docos-10-enedioic acid	64°	73—74°
Wt. oxidised (g.)	0·851	0·872
Wt. (g.) of crude dihydroxy-acid	0·695	0·692
M. p. of pure dihydroxy-acid	154—155°	127·5—128·5°
Found (%)	C, 65·7; H, 10·2	C, 66·0; H, 10·3

Calc. for $C_{22}H_{42}O_6$: C, 65·6; H, 10·5%.

Acetone–permanganate oxidations were carried out on the ester fractions (*a*) S_1, (*b*) L_2, L_3, L_4, and L_5 combined (*cis*-ester), and (*c*) S_5 (*trans*-ester). The dibasic acids obtained in (*b*) and (*c*) were then converted into methyl esters and distilled. Results are as below. The ester fractions thus obtained were hydrolysed and the acids examined.

Fraction 5C3 (0·62 g.), on repeated crystallisation from water, chloroform and ethyl acetate, yielded sebacic acid (0·06 g.), m. p. and mixed m. p. 130°.

Fraction 5C5 (0·41 g.) on crystallisation from hot water and ethyl acetate yielded dodecanedioic acid (0·02 g.), m. p. and mixed m. p. 127°. A further fraction had m. p. 106—108°, not identical with undecanedioic acid, m. p. 109°.

Fraction 5T3 (0·41 g.) on repeated crystallisation from water, ethyl acetate, and chloroform gave sebacic acid (0·02 g.), m. p. and mixed m. p. 129°. A further fraction had m. p. 110° (mixed with undecanedioic acid, 94°).

Fraction	S_1	*cis* (L_2—L_5)	*trans* (S_5)
Wt. oxidised (g.)	5·69	5·78	4·27
Wt. of unoxidised ester (g.)	1·85	0·56	0·14
Wt. of dibasic acids (g.)	—	4·76	3·92

Dimethyl esters.

cis			*trans*		
Fraction	Wt. (g.)	Sap equiv.	Fraction	Wt. (g.)	Sap. equiv.
5C1	0·909	111·1	5T1	0·407	112·3
5C2	0·711	113·8	5T2	0·505	113·5
5C3	0·739	116·4	5T3	0·518	115·1
5C4	1·066	119·6	5T4	0·537	117·8
5C5	0·499	122·8	5T5	0·631	119·4
5C6	0·326	130·0	5T6	0·716	124·0
			5T7	0·214	141·1
Total	4·250		Total	3·528	

Fraction 5T6 (0·54 g.), by crystallisation from water and ethyl acetate, yielded dodecanedioic acid (0·17 g.), m. p. and mixed m. p. 127°. A more soluble fraction had m. p. 108—110° but was not identical with undecanedioic acid.

Fraction 6. This (5·3 g.; I.V. 0·6), crystallised from acetone (53 ml.) at room temperature, yielded dimethyl docosanedioate (4·74 g.), m. p. 71° (Found: C, 72·2; H, 11·4%; sap. equiv., 197·6. Calc. for $C_{24}H_{46}O_4$: C, 72·3; H, 11·6%; sap. equiv., 198·2). The acid (0·78 g.; m. p. 125—126°) recovered after hydrolysis of the dimethyl ester (0·98 g.) was recrystallised from alcohol (140 ml.) at room temperature and gave docosanedioic acid (0·63 g.), m. p. 125—125·5°. Published m. p.s vary notably for the acid (120—122° to 126·9—127·1°) and its dimethyl ester (67—68° to 70·2—71°).

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THE UNIVERSITY, LIVERPOOL. [*Received, February 4th*, 1953.]

454. *Magnetic Properties and Structure of Copper Laurate.*

By A. GILMOUR and R. C. PINK.

Copper laurate has a maximum magnetic susceptibility at approximately 230° K, the experimental data indicating that at 35° K, the paramagnetic contribution to the susceptibility would be zero. This is explained by assuming the existence of strong quantum-mechanical exchange forces between the copper atoms. A covalent chelate structure for copper laurate is suggested, based on magnetic and chemical evidence provided by measurements on copper laurate and its co-ordination compounds with ammonia and pyridine.

ALTHOUGH early measurements of the magnetic susceptibility of copper soaps revealed no abnormal behaviour (Bhatnagar, Singh, and Ghani, *Indian J. Phys.*, 1932, **7**, 323), subsequent measurements have indicated that the magnetic moment of the copper in these compounds is anomalously low. Thus, Amiel (*Compt. rend.*, 1938, **207**, 1097), found for the molar susceptibility of copper in copper laurate at 20° a value of only $0·875 \times 10^{-3}$ c.g.s.u. in contrast to the value of $1·700 \times 10^{-3}$ c.g.s.u. in hydrated copper sulphate. In view of the difficulty of obtaining pure metal soaps (cf. Elliott, "The Alkaline Earth and Heavy Metal Soaps," Reinhold Publishing Corp., New York, 1946) information on the purity of the materials used in these investigations is unfortunately not available.

The present measurements confirm the anomalously low value reported by Amiel and show further that copper laurate becomes anti-ferromagnetic at low temperatures. Susceptibility data for complexes of copper laurate with ammonia and pyridine are also reported.

These measurements throw some light on the nature of the bonding in the copper soaps which is in accord with other evidence.

Experimental

Preparation and Analysis of Materials.—The lauric acid was a pre-war " purissimus grade " sample from Schering-Kahlbaum (m. p. 44·1°). Copper laurate was prepared by metathesis of sodium laurate in 60% ethanol with an aqueous solution of copper sulphate at 40°. The precipitated soap was set aside overnight and then washed repeatedly on a sintered-glass filter with aqueous ethanol to remove excess of precipitant and free fatty acid. After drying in an air oven at 80° for 2 hr. the product was recrystallised from warm carbon tetrachloride and finally dried *in vacuo*. It was stored over phosphoric oxide (Found : Cu, 13·5, 13·6. Calc. for $C_{24}H_{46}O_4Cu$: Cu, 13·8%). Preparation of copper laurate was also attempted by Amiel's method (*loc. cit.*) in which the fatty acid is added to a cuprammonium solution containing potassium hydroxide. The violet precipitate obtained in this way, proved to be the diammine (Found : NH_3, 6·9. Calc. for $C_{24}H_{46}O_4Cu,2NH_3$: NH_3, 6·85%). This complex lost ammonia readily when warmed, yielding a product identical with that obtained by direct metathesis. The diammine was also obtained by passing ammonia into a solution of copper laurate in chloroform. A bright green monopyridine complex of copper laurate (Found : C_5H_5N, 14·6. Calc. for $C_{24}H_{46}O_4Cu,C_5H_5N$: C_5H_5N, 14·6%) was similarly obtained by adding pyridine to a chloroform solution of the soap. Although pyridine solutions of copper laurate are blue, attempts to isolate a stable dipyridine complex were not successful. A solution of copper laurate in dry pyridine yielded a very small quantity of violet-blue platelets after 48 hr. at 0° but this product rapidly lost pyridine, yielding the green monopyridine complex. No magnetic measurements were made with the violet-blue product.

For analysis, copper laurate was hydrolysed with 2N-sulphuric acid, and the copper in the hydrolysate estimated gravimetrically as dipyridinecopper dithiocyanate, after the free fatty acid had been removed by filtration. Ammonia and pyridine in the complexes were estimated by determining the loss in weight after heating them at 80° to constant weight.

Magnetic Measurements.—Susceptibility measurements were made by the Gouy method with an apparatus described previously (McDonnell, Pink, and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 156). The only modification was the provision of a heater winding on the brass jacket so that measurements could be made above room temperature. The current for the heater was supplied by an electronically stabilised power unit which permitted temperature control of the Gouy tube to $\pm 0{\cdot}2°$. The measurements at 90° K and 190° K were made in an atmosphere of nitrogen. At least three completely separate measurements were made with each sample. With the powdered specimens the accuracy, which was limited by the reproducibility of packing, was estimated to be $\pm 1\%$. The magnetic data are summarised in the Table, which gives the molar susceptibility of copper at 291° K (χ_{Cu}) in each of the compounds studied.

	$10^6\chi_{Cu}$, c.g.s.u.		$10^6\chi_{Cu}$, c.g.s.u.
Copper sulphate pentahydrate	1·700	Copper laurate monopyridine complex	0·928
Copper laurate	0·954	Copper laurate in pyridine solution ...	1·648
Diamminocopper laurate	1·761		

The values shown have been corrected for the diamagnetic contribution to the susceptibility from the organic part of the molecule. Standard Pascal corrections were employed throughout. The value for solid copper sulphate pentahydrate, which has been shown to obey the Curie–Weiss law almost perfectly down to 14° K, is included in the Table for comparison. The variation of χ_{Cu} in copper laurate with temperature is shown in Fig. 1.

Volatility of Copper Laurate.—When copper laurate was heated in a molecular still at pressures $< 10^{-4}$ mm. small quantities of a blue product, which appeared to be identical with copper laurate, were obtained (Found : Cu, 13·6, 12·4, 14·5%). Approximately 10 mg. were obtained after 5 hours' distillation at 200—210° with a still path of 1 cm. At higher temperatures considerable darkening occurred and a paler material was obtained which appeared to contain a proportion of copper-free products.

Discussion

The most important observation is the rapid fall in the paramagnetic susceptibility of copper laurate below 230° K. Extrapolation of the experimental data indicates that, at 35° K, the paramagnetic contribution to the measured susceptibility would be zero (Fig. 1). In copper compounds which obey the Curie–Weiss law, like copper sulphate

pentahydrate, the measured susceptibility can be accounted for on the basis of a contribution to the magnetic moment from the spin only, the orbital moment being effectively quenched by the interatomic forces (Van Vleck, " Theory of Electric and Magnetic Susceptibilities," Clarendon Press, Oxford, 1932). In copper laurate below room temperature a mechanism for quenching the spin must also be found. While internal magnetic coupling between the spin and orbit provides a possible mechanism (Van Vleck, *loc. cit.*), it seems more likely that quenching occurs through the existence of sufficiently strong exchange forces between the copper atoms to aline the spins into an antiparallel and therefore diamagnetic state. At higher temperatures, states with higher energies will be favoured and a proportion of the spins will remain uncoupled. These uncoupled spins will contribute to the paramagnetic susceptibility and give rise to the normal negative temperature coefficient of susceptibility observed above 230° K. A similar explanation has been advanced recently by Bleaney and Bowers (*Proc. Roy. Soc.*, 1952, *A*, **214**, 451), to account for the anomalous susceptibility and paramagnetic resonance spectrum of hydrated copper acetate. Although detailed *X*-ray data for copper laurate are not available, Vold and Hattiangdi (*Ind. Eng. Chem.*, 1949, **41**, 2311), have shown that the crystal structure in a large number of heavy-metal soaps has the characteristic features illustrated in Fig. 2. The

FIG. 1. *Effect of temperature on the magnetic susceptibility of copper (χ_{Cu}) in copper laurate.*

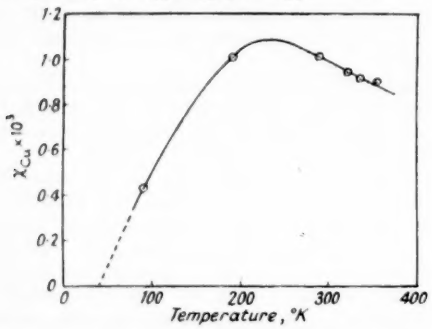
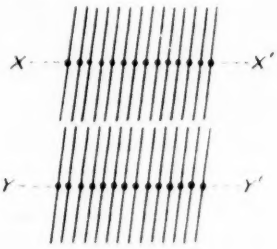


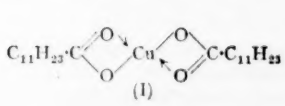
FIG. 2. *Metal soap lattice.*

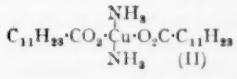


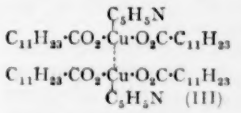
metal ions are arranged in planes, between which the fatty acid radicals extend in both directions, with their axes slightly inclined to the planes containing the metal-carboxylate groups. The feature of this structure which is of importance, in the present connection, is the very high localised concentration of metal atoms along the planes XX', YY'. In copper acetate, Bleaney and Bowers (*loc. cit.*) postulated exchange forces between isolated pairs of copper ions. In copper laurate, on the other hand, the markedly anisotropic character of such a lattice might permit co-operative effects along the planes XX', YY', which extend throughout the crystal. In this sense the phenomenon may properly be referred to as anti-ferromagnetism.

The chemical evidence is also in favour of an explanation based on strong interatomic exchange forces. In the neutral copper atom the lowest level of the spectrum is a ^2S term and the Cu^+ ion is therefore diamagnetic. Formation of a Cu^{++} ion involves excitation of the copper atom to the ^2D level, the relative ease of obtaining the cupric ion in solution being attributed to the heat of hydration, which supplies the necessary energy for the excitation process. Also, Joos (*Ann. Physik*, 1926, **81**, 1076; 1928, **85**, 641) has emphasised that the colour of solutions containing elements of the iron group must be associated with transitions between different energy levels of complexes, as the metal ions have no normal absorption lines softer than 1300 Å. Since cupric laurate is not hydrated, but is strongly coloured, it seems probable that the necessary energy required to stabilise the copper in the cupric state is provided by internal co-ordination of the type shown in (I). In this chelate structure the covalent bonding would permit the close approach of the metal atoms necessary for the full development of the exchange forces. In most salts of the transition-group elements, these forces are of subordinate importance because of the

distance between the paramagnetic centres which results from the high dilution with diamagnetic atoms or ions. Niekerk and Schoennig (*Nature*, **1953**, **171**, 37) have reported that the Cu–Cu distance in hydrated copper acetate is 2·64 Å which is only slightly greater


(I)


(II)


(III)

than the value 2·56 Å found in metallic copper. The fact that the susceptibility of copper acetate is closely similar to that of copper laurate (Amiel, *loc. cit.*) supports the suggestion that the copper atoms in copper laurate are sufficiently close for the exchange forces to play an important part in the susceptibility. It should be noted that chelation alone does not account for the anomalously low susceptibility of copper laurate below 230° K. The electronic configuration of cupric copper either in the ionic state or in the covalent planar (dsp^2) or tetrahedral (sp^3) states, involves one unpaired electron. Co-ordinated cupric copper is therefore paramagnetic unless other forces intervene to quench the spin component.

The ready solubility of copper laurate in a number of organic solvents and the relative ease with which copper laurate can be volatilised, *in vacuo*, provide additional evidence for the chelate structure (I). Magnetic data for the ammonia and pyridine complexes are also consistent with this hypothesis. In the blue diammine, $Cu(C_{11}H_{23}\cdot CO_2)_2,2NH_3$ (II), close approach of the copper carboxylate groups will be prevented by the co-ordinated ammonia molecules and the copper should exert its normal spin moment. In the green monopyridine complex, on the other hand, the low susceptibility indicates that close approach of pairs of copper atoms is possible as in copper acetate. A structural unit consisting of two molecules of the monopyridine complex is therefore likely (III), but has not been confirmed. Since pyridine solutions of copper laurate are blue and since, in these solutions, the soap is known to be dispersed as single molecules (Nelson and Pink, *J.*, 1952, 1744) the susceptibility derived from measurements with pyridine solutions might be expected to approach the normal spin-only value. The data in the Table fully confirm these expectations and provide supporting evidence both for the chelate structure (I) and for the proposed mechanism for the quenching of the spin moment in copper laurate at low temperatures.

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455. *Anionotropic Systems. Part II.* Syntheses and Rearrangements in the* cyclo*Heptenyl Series.*

By E. A. Braude, W. F. Forbes, and (in part) E. A. Evans.

In continuation of earlier work, the study of anionotropic rearrangements in *cyclo*olefinic systems has been extended to the *cyclo*heptenyl series.

Four *cyclo*hept-1-enylcarbinols containing different unsaturated side-chains have been synthesised by the reaction of *cyclo*hept-1-enyl-lithium (the constitution of which is proved by carboxylation) with benzaldehyde, acraldehyde, crotonaldehyde, and sorbaldehyde. The acid-catalysed isomerisations of the carbinols are described. It is found that the rearrangements of the vinyl and the propenyl derivatives take opposite courses, in agreement with the observations previously made in the *cyclo*pentenyl and *cyclo*hexenyl series.

In earlier papers (Braude and Coles, *J.*, 1950, 2014; Braude and Forbes, 1951, 1755; Braude, Bruun, Toogood, and Weedon, 1952, 1414, 1419), investigations on the anionotropic rearrangements of *cyclo*pentenyl- and *cyclo*hexenyl-carbinols were described. These studies have now been extended to the seven-membered series, both for their synthetic interest in providing routes to a variety of *cyclo*heptenyl derivatives (cf. *Nature*, 1951, **168**, 874; *J.*, 1953, 2208) and for kinetic studies, which will be reported later, on the relation between ring size and reactivity in *cyclo*olefinic systems.

As previously, the method of direct alkenylation proved highly convenient. Conversion of 1-chloro*cyclo*heptene, obtained in good yield from *cyclo*heptanone with phosphorus pentachloride (cf. Favorskii and Domnin, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 727), into *cyclo*heptenyl-lithium presented no difficulty. The rate of metalation of the carefully purified chloro*cyclo*heptene is somewhat slower than that of the six-membered analogue (Braude and Coles, *loc. cit.*) but overall yields of up to 60% were obtained in the addition reactions described below. The constitution of the lithium alkenyl was established by carboxylation which gave the known *cyclo*hepten-1-enylcarboxylic acid (Dele, Schorlemmer, and Spiegel, *J.*, 1881, 541; Willstätter, *Annalen*, 1901, **317**, 237) as well as di*cyclo*heptenyl ketone (I) which was characterised by a 2 : 4-dinitrophenylhydrazone and converted into di*cyclo*heptyl ketone by catalytic hydrogenation. On treatment with formic and phosphoric acids, di*cyclo*heptenyl ketone underwent cyclisation to the tricyclic ketone (II) (cf. Braude and Coles, *J.*, 1952, 1430).

Reaction of *cyclo*heptenyl-lithium with benzaldehyde, acraldehyde, crotonaldehyde, and sorbaldehyde afforded the secondary alcohols (III, VI, and XII; $n = 1$) and (XII; $n = 2$), all liquids at room temperature. Their structures are confirmed by the ultraviolet light absorptions and by the reactions described below. The alcohol (XII; $n = 1$) was also hydrogenated catalytically to 1-*cyclo*heptylbutan-1-ol.

With Brady's reagent, (III) undergoes oxidation to *cyclo*heptenyl phenyl ketone, which is isolated as the 2 : 4-dinitrophenylhydrazone in about 50% yield. The ease of this interesting reaction appears to be markedly greater in the present case than in those previously described (Braude and Forbes, *J.*, 1951, 1762).

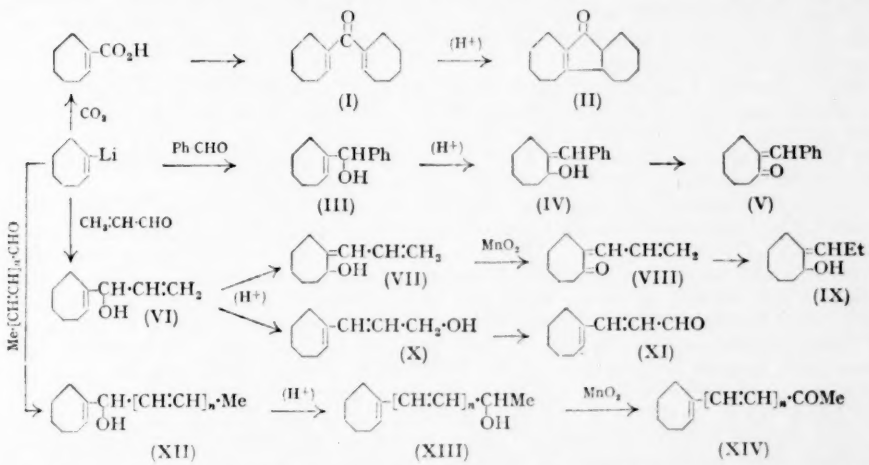
Anionotropic rearrangements of the alcohols (III), (VI), and (XII) to the fully conjugated isomers were effected in practically quantitative yields by treatment with dilute hydrochloric acid in aqueous dioxan or acetone at room temperature. α-*cyclo*Hept-1′-enylbenzyl alcohol (III) gave 2-benzylidene*cyclo*heptanol (IV), which exhibits ultraviolet light absorption typical of a styryl derivative. It was oxidised, most conveniently with chromium trioxide in pyridine (Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422), to 2-benzylidene*cyclo*heptanone (V). The latter was also prepared directly from *cyclo*heptanone by condensation with benzaldehyde, and could be converted into (IV) by reduction with lithium aluminium hydride.

The rearrangement of 1-*cyclo*hept-1′-enylallyl alcohol (VI) gave exclusively 2-allyl-

* Part I, *J.*, 1953, 419.

idene*cyclo*heptanol (VII). Complete absence of the alternative isomerisation product (X) was proved by oxidation with manganese dioxide which gave 2-allylidene*cyclo*heptanone (VIII) but no trace of the aldehyde (XI), as shown by a negative Schiff's test. The structures of (VII) and (VIII) were confirmed by their ultra-violet light absorptions (see Table) and by catalytic hydrogenation to 2-*n*-propyl*cyclo*heptanol and 2-*n*-propyl*cyclo*heptanone. The latter was identified by the 2 : 4-dinitrophenylhydrazone which was identical with the derivative of an authentic sample of the ketone obtained by ring-expansion of *cyclo*hexanone with diazo-*n*-butane (cf. Adamson and Kenner, *J.*, 1939, 181; Cook, Raphael, and Scott, *J.*, 1951, 695). The course of the hydrogenation of 2-allylidene*cyclo*heptanone was not completely selective, however, and the main product was admixed with an isomer. This was probably 2-propylidene*cyclo*heptanol (IX); its infra-red light absorption resembled that of 2-propyl*cyclo*heptanol, but showed additional peaks at 1615 and 860 cm.$^{-1}$ which can be ascribed to C=C stretching and C–H bending vibrations of a trialkylated ethylenic group.

In contrast to (VI), the higher homologue, 1-*cyclo*hept-1′-enylbut-2-en-1-ol (XII; $n = 1$), undergoes rearrangement with migration of the hydroxyl group in the opposite direction to give 4-*cyclo*hept-1′-enylbut-3-en-2-ol (XIII; $n = 1$). The structure of the rearrangement product was proved by oxidation with manganese dioxide to the corresponding diene ketone (XIV; $n = 1$) which had previously been prepared by a different route by Heilbron, Jones, Toogood, and Weedon (*J.*, 1949, 1827) and was identified by the 2 : 4-dinitrophenylhydrazone. The latter was also obtained directly from (XIII; $n = 1$) by treatment with Brady's reagent. The opposite directions of rearrangement of the vinylcarbinol (VI) and the propenylcarbinol (XII; $n = 1$) correspond to the observations



previously made in the *cyclo*pentenyl and *cyclo*hexenyl series (Braude and Coles, 1950; Braude and Forbes, 1951, *locc. cit.*) and no change in behaviour with increasing ring-size is expected or found.

The rearrangement of 1-*cyclo*hept-1′-enylhexa-2 : 4-dien-1-ol (XII; $n = 2$) gave an isomer, the ultra-violet light absorption of which shows that all three ethylenic bonds have become conjugated (see Table). The structure of the product was not rigidly established, but by analogy with the corresponding *cyclo*hexenyl derivatives (Braude, Brunn, Weedon, and Woods, 1952, *loc. cit.*), the direction of migration is again almost certainly along the side-chain to give (XIII; $n = 2$). Direct treatment of (XIII; $n = 2$) with Brady's reagent gave a 15% yield of the 2 : 4-dinitrophenylhydrazone of the corresponding triene ketone (XIV; $n = 2$).

The ultra-violet light absorptions of the *cyclo*heptenyl derivatives show certain significant differences from those of the *cyclo*hexenyl derivatives (Braude and Coles, 1950, *loc. cit.*),

Ultra-violet light absorption of cyclo*heptenyl derivatives* (*in ethanol*).

	$\lambda_{max.}$, Å	$\varepsilon_{max.}$		$\lambda_{max.}$, Å	$\varepsilon_{max.}$
*cyclo*Hept-1-enecarboxylic acid	2130	11,200	4-*cyclo*Hept-1′-enylbut-3-en-2-ol (XIII; $n = 1$)	2390	23,500
Di*cyclo*hept-1-enyl ketone (I)	2450	6,000			
	3200	100	4-*cyclo*Hept-1′-enylbut-3-en-2-one (XIV; $n = 1$)	2410	4,500
				2810	18,000
tricyclo[8 : 5 : $0^{3,9}$]Pentadec-1(10)-en-2-one (II)	2420	12,500		2880	18,000
	3020	100			
			6-*cyclo*Hept-1′-enylhexa-3 : 5-dien-2-ol (XIII; $n = 2$)	2290	6,000
2-Benzylidene*cyclo*heptanol (IV)	2470	12,100		2700	12,000
				2800	14,500
2-Allylidene*cyclo*heptanol (VII)	2360	22,000		2880	12,000
2-Allylidene*cyclo*heptanone (VIII)	2700	15,000			
	2800	15,000			

but more detailed discussion is deferred until work now in progress on higher-membered *cyclo*alkenyl systems is completed.

Experimental

Analytical data were determined in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. I. A. Boston) laboratories of this Department.

cyclo*Hept*-1-*enyl-lithium*.—*cyclo*Heptanone (285 ml.) was slowly added to phosphorus pentachloride (500 g.), with stirring and external cooling. After 3 hr., the products were added dropwise to ice-water (4 l.), and the mixture was extracted with ether (1 l.). The ethereal layer was separated, dried ($CaCl_2$), and fractionated through an electrically heated, 8″ Fenske column, giving 1-chloro*cyclo*heptene (235 g., 70%) as a colourless liquid, b. p. 75°/26 mm., n_D^{21} 1·4844 (Found : Cl, 27·2. Calc. for $C_7H_{11}Cl$: Cl, 27·1%). (Favorskii and Domnin, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 340, give b. p. 58—59°/12 mm.) The chloride is reasonably stable at 0°; it gives no immediate reaction with alcoholic silver nitrate, but a precipitate of silver chloride is formed slowly.

Freshly distilled 1-chloro*cyclo*heptene (65 g., 0·5 mole) in ether (100 ml.) was slowly added to a stirred suspension of finely-cut lithium (6·9 g., 1 g.-atom) in sodium-dried ether (500 ml.) under nitrogen. The mixture was then heated under gentle reflux. Reaction usually set in after 1—2 hr. and was complete after 6—12 hr., almost the whole of the metal being consumed. The solution of *cyclo*hept-1-enyl-lithium has a greenish-grey colour.

cyclo*Hept*-1-*enecarboxylic Acid and Di*cyclo*hept*-1-*enyl Ketone*.—Excess of solid carbon dioxide (200 g.) was added to a solution of 1-*cyclo*heptenyl-lithium (from Li, 6·6 g.), with cooling in methanol–solid carbon dioxide. After 6 hr., the solution was acidified with aqueous hydrochloric acid, and the ethereal layer was separated. Extraction with aqueous sodium hydrogen carbonate and working up in the usual way gave *cyclo*hept-1-enecarboxylic acid (2 g., 3%) which, after distillation at 130° (bath)/10^{-5} mm., crystallised from methanol in plates, m. p. 49° (Dele, Schorlemmer, and Spiegel, *J.*, 1881, 541, give m. p. 53—54°), and formed an amide, plates (from aqueous methanol), m. p. 157° (Willstätter, *Annalen*, 1901, **317**, 237, gives m. p. 158—159°). The ethereal layer was dried (Na_2SO_4) and fractionated, giving *di*cyclo*hept*-1-*enyl ketone* (11 g., 21%), b. p. 116°/2 × 10^{-4} mm., n_D^{21} 1·5230 (Found : C, 82·8; H, 10·4. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Light absorption : see Table. The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, separated from ethyl acetate in prisms, m. p. 200° (Found : C, 63·5; H, 6·7; N, 13·7. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·5; N, 14·05%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3980 Å, ε 26,800.

*Di*cyclo*heptyl Ketone*.—The ketone (2 g.) in ethanol (40 ml.) in the presence of platinic oxide absorbed 220 ml. of hydrogen at 17°/750 mm. (Calc., 220 ml.), giving *di*cyclo*heptyl ketone*, b. p. 110°/5 × 10^{-3} mm., n_D^{21} 1·5030 (Found : C, 81·5; H, 11·5. $C_{15}H_{26}O$ requires C, 81·0; H, 11·8%). The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, separated from ethyl acetate in orange needles, m. p. 95° (Found : N, 13·55. $C_{21}H_{30}O_4N_4$ requires N, 13·9%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3700 Å, ε 24,000.

tricyclo[8 : 5 : $0^{3,9}$]*Pentadec*-1(10)-*en*-2-*one* (II).—Di*cyclo*heptenyl ketone (7 g.) was cautiously added to a mixture of phosphoric acid (2 g.) and formic acid (8 g.) at 0°. Next day, the mixture was heated at 90° for 6 hr., then cooled, diluted with ice-water (200 ml.), and extracted with ether. The ethereal layer was washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and fractionated, giving the tricyclo-*ketone* (5 g.) as a colourless liquid, b. p. 200° (bath)/10^{-5} mm., which solidified and crystallised from light petroleum (b. p. 40—60°) in colourless plates,

m. p. 43° (Found : C, 82·1; H, 10·1. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Light absorption : see Table. The 2 : 4-*dinitrophenylhydrazone*, after chromatography in benzene–chloroform on alumina, crystallised from ethyl acetate in fine orange-red needles, m. p. 171° (Found : N, 13·7. $C_{21}H_{26}O_4N_4$ requires N, 14·05%). Light absorption in $CHCl_3$: Max. at 3980 Å, ε 29,500.

α-cyclo*Hept*-1′-*enylbenzyl Alcohol* (III).—Freshly distilled benzaldehyde (40 g.) in ether (50 ml.) was added dropwise to a stirred solution of *cyclo*hept-1-enyl-lithium (from Li, 5·2 g.). After 12 hr., saturated aqueous ammonium chloride (500 ml.) was added and the ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated from a trace of potassium carbonate, giving α-cyclo*hept*-1′-*enylbenzyl alcohol* (37 g., 48%) as a colourless liquid, b. p. 94°/2 × 10^{-3} mm., n_D^{24} 1·5429 (Found : C, 83·2; H, 9·1. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption in EtOH : $\lambda_{max.}$ 2470 Å, ε 2000.

When α-*cyclo*hept-1′-enylbenzyl alcohol (2 g.) was warmed with 2 : 4-dinitrophenylhydrazine (2·6 g.), concentrated sulphuric acid (6 ml.), ethanol (40 ml.), and water (10 ml.) for 5 min. on the water-bath, cyclo*heptenyl phenyl ketone* 2 : 4-*dinitrophenylhydrazone* (1·9 g., 50%) was gradually precipitated. After chromatography on alumina in benzene–chloroform, it crystallised from ethyl acetate in red needles (1·5 g.), m. p. 131° (Found : C, 63·0; H, 5·6; N, 14·6. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 30,600. The yield of hydrazone is considerably higher than observed in other cases (Braude and Forbes, *J.*, 1951, 1762). The m. p. was not depressed on admixture with a specimen prepared from the ketone (Braude and Forbes, following paper).

2-*Benzylidene*cyclo*heptanol* (IV).—The above alcohol (16 g.) was dissolved in a 0·1M-solution of hydrogen chloride in 80% aqueous acetone (400 ml.). After 3 days at room temperature, the solution was neutralised with potassium carbonate and most of the acetone was distilled off through a column. The remaining solution was extracted with ether, and the ethereal layer was dried (K_2CO_3–Na_2SO_4) and fractionated, giving 2-*benzylidene*cyclo*heptanol* (15 g.), b. p. 102°/5 × 10^{-4} mm., n_D^{20} 1·5653 (Found : C, 82·8; H, 8·9. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption : see Table. The p-*nitrobenzoate* crystallised from light petroleum (b. p. 40—60°)–methanol in needles, m. p. 185° (Found : N, 3·9. $C_{21}H_{21}O_4N$ requires N, 4·0%).

2-*Benzylidene*cyclo*heptanone* (V).—(*a*) A mixture of *cyclo*heptanone (5·6 g.), benzaldehyde (5·3 g.), methanol (20 ml.), and 10N-NaOH (2 ml.) was kept for 15 hr. at 20°. After dilution with water (100 ml.), the products were isolated with ether and distilled. A mixture (4 g.), b. p. 125°/10^{-2} mm., n_D^{19} 1·5560—1·5660 was obtained, consisting of 2-benzylidene*cyclo*heptanone and 2-α-hydroxybenzyl*cyclo*heptanone. Refractionation from a trace of naphthalene-2-sulphonic acid gave pure 2-*benzylidene*cyclo*heptanone* (3·6 g.), n_D^{20} 1·5868, which crystallised from pentane in plates, m. p. 37·5° (Found : C, 83·8; H, 8·2. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0%). Light absorption : Max. at 2700, 2810, and 2900 Å; ε 13,500, 14,500, and 14,000 in EtOH; 2710 and 2800 Å, ε 15,000 in *n*-hexane. The solution in ethanol is unstable, probably because of the formation of 2-α-ethoxybenzyl*cyclo*heptanone. The 2 : 4-*dinitrophenylhydrazone* was chromatographed on alumina in benzene–chloroform, and crystallised from ethyl acetate–methanol in red needles, m. p. 158° (Found : C, 62·8; H, 5·6; N, 14·65. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: Max. at 3780 Å; ε 25,000.

(*b*) 2-Benzylidene*cyclo*heptanol (1·2 g.) in dry pyridine (15 ml.) was added to chromium trioxide (1·5 g.) and pyridine (15 ml.). The mixture was kept for 12 hr. at 20° and then added to water (200 ml.) and extracted with ether. The ethereal extracts were washed with 2N-hydrochloric acid and water, dried (Na_2SO_4), and then fractionated, giving 2-benzylidene*cyclo*heptanone (1 g.), b. p. 117—118°/10^{-2} mm., m. p. 37° (from pentane) undepressed on admixture with the authentic specimen described above. It formed a 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158°.

Reduction of the ketone (0·4 g.) with lithium aluminium hydride (0·7 g.) in ether at 20° reconverted it into the 2-benzylidene*cyclo*heptanol (0·3 g.), b. p. 80° (bath-temp.)/10^{-5} mm., n_D^{23} 1·5775, $\lambda_{max.}$ 2480 Å, ε 12,300, which gave no precipitate on treatment with Brady's reagent.

1-cyclo*Hept*-1′-*enylallyl Alcohol* (VI).—Freshly distilled acraldehyde (35 g.) in ether (50 ml.) was added dropwise to a stirred, ethereal solution of *cyclo*hept-1-enyl-lithium (from Li, 6·9 g.) at 0°. After a further 3 hr.' stirring at room temperature, saturated aqueous ammonium chloride was added and the products were worked up as described above, giving the *allyl alcohol* (35 g., 46%), b. p. 63°/0·5 mm., n_D^{20} 1·4990 (Found : C, 79·0; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption in EtOH : ε <750 between 2200 and 3000 Å.

2-*Allylidene*cyclo*heptanol* (VII).—The above alcohol (8 g.) was dissolved in a 0·05M-solution of hydrogen chloride in 60% aqueous acetone (200 ml.). After 14 hr. at room temperature, the products were worked up as described above, giving 2-*allylidene*cyclo*heptanol* (7 g.), b. p.

83°/0·5 mm., n_D^{20} 1·5071 (Found: C, 79·2; H, 10·7. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). Light absorption: see Table. The **3**: 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in plates, m. p. 77° (Found: C, 58·7; H, 5·3; N, 8·2. $C_{17}H_{18}O_6N_2$ requires C, 59·0; H, 5·2; N, 8·1%). Light absorption in EtOH: $\lambda_{max.}$ 2300 Å, ε 43,000; $\lambda_{infl.}$ 2370 Å, ε 42,000.

2-Allylidene*cyclo*heptanol (6·5 g.) in absolute ethanol (50 ml.) in the presence of platinic oxide absorbed 1390 ml. of hydrogen at 21°/768 mm. (Calc., 1400 ml.), giving (*trans*?-)2-*n*-propyl*cyclo*heptanol (6 g.), b. p. 67°/0·5 mm., n_D^{22} 1·4702. Infra-red light absorption: Max. at 3350—3450 (s), 1460 (s), 1025 (s), and 925 (m) cm.$^{-1}$. It formed a 3: 5-*dinitrobenzoate*, prisms [from light petroleum (b. p. 60—80°)], m. p. 90—91° (Found: C, 58·0; H, 6·4; N, 8·4. $C_{17}H_{22}O_6N_2$ requires C, 58·3; H, 6·3; N, 8·0%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å (ε 23,000); $\lambda_{infl.}$ 2370 Å (ε 20,500).

2-*Allylidene*cyclo*heptanone* (VIII).—2-Allylidene*cyclo*heptanol (15 g.), vacuum-dried manganese dioxide (150 g.), and sodium-dried light petroleum (b. p. 40—60°) were shaken under nitrogen for 3 days at room temperature. The mixture was filtered, and the filtrate and washings were fractionated. The product gave no colour with Schiff's reagent and was 2-*allylidene*cyclo*heptanone* (12 g.), b. p. 46°/0·1 mm., n_D^{22} 1·5358 (Found: C, 79·7; H, 9·7. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%). Light absorption: see Table. The 2: 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red, monoclinic needles, m. p. 158—159° (Found: N, 16·95. $C_{16}H_{18}O_4N_4$ requires N, 16·95%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3840 Å, ε 19,000.

In absolute ethanol (70 ml.) in the presence of platinic oxide (200 mg.) the ketone (10·7 g.) absorbed 2400 ml. of hydrogen during 48 hr. at 20°/772 mm. (Calc. for 2 mols., 3400 ml.). Fractionation of the product gave a series of fractions (total, 10 g.) ranging from b. p. 42°/0·1 mm., n_D^{21} 1·4705 (Found: C, 77·8; H, 11·9. Calc. for $C_{10}H_{18}O$: C, 77·9; H, 11·8%), to b. p. 48°/0·1 mm., n_D^{21} 1·4800 (Found: C, 77·7; H, 12·0%), which consisted of mixtures of 2-*n*-propyl*cyclo*heptanone and an isomer, probably 2-propylidene*cyclo*heptanol. The infra-red spectrum of the lowest-boiling fraction was almost identical with that of an authentic sample of the saturated ketone (see below), whereas the infra-red spectrum of the highest-boiling fraction showed maxima at 3350—3450 (s) (O–H stretching), 1616 (w), 1460 (s), 1042 (s) (C–O stretching; cf. Zeiss and Tsutsu, *J. Amer. Chem. Soc.*, 1953, **75**, 897), 999 (s), and 860 (w) cm.$^{-1}$. The spectra of the middle fractions were intermediate in character. The highest-boiling fraction contained 0·48% of active hydrogen (Zerewitinoff) (Calc. for propylidene*cyclo*heptanol, 0·65%). On treatment with 2: 4-dinitrophenylhydrazine in ethanol–sulphuric acid, each fraction gave 2-*n*-propyl*cyclo*heptanone 2: 4-dinitrophenylhydrazone (total, 4·9 g., 23%), m. p. 90—92°, undepressed on admixture with the authentic sample described below. The derivative (1 g.) was warmed with chloroform (20 ml.), pyruvic acid (27 ml.), and a solution of hydrogen bromide in acetic acid (2·3N; 2·2 ml.) for 2·5 hr. at 45° with occasional shaking, and the mixture extracted with aqueous sodium hydrogen carbonate (cf. Mattox and Kendall, *J. Amer. Chem. Soc.*, 1948, **70**, 882). The regenerated 2-*n*-propyl*cyclo*heptanone had b. p. 50°/0·5 mm., n_D^{21} 1·4569, and formed a semicarbazone, m. p. 137°, undepressed on admixture with the authentic specimen described below.

2-n-*Propyl*cyclo*heptanone*.—(*a*) *N*-Nitroso-*n*-butylurethane (91 g.), prepared from *n*-butylurethane by the method of Cook, Raphael, and Scott (*J.*, 1951, 695), was added slowly to a stirred mixture of *cyclo*hexanone (53·3 g.), methanol (57 ml.), and sodium carbonate (1 g.) at 20—25°. Next day, the mixture was filtered and the filtrate fractionated, giving 2-n-*propyl*cyclo*heptanone* (40 ml.), b. p. 50°/0·5 mm., n_D^{24} 1·4553 (Found: C, 77·7; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%). Infra-red light absorption: Max. at 3340 (m) (C = O stretching overtone), 1700 (s) (C = O stretching), 1460 (s), and 933 (s) cm.$^{-1}$. The *semicarbazone* crystallised from methanol in plates, m. p. 137—138° (Found: N, 19·9. $C_{11}H_{21}ON_3$ requires N, 19·9%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å, ε 15,400. The 2: 4-*dinitrophenylhydrazone*, after chromatography on alumina in benzene–chloroform, crystallised from ethyl acetate in red needles, m. p. 90—91° (Found: C, 57·9; H, 6·6; N, 17·1. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6; N, 16·8%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3680 Å, ε 25,000.

The ketone was recovered unchanged when an ethanol solution was shaken with platinum oxide in hydrogen at room temperature.

(*b*) The ketone was also obtained, in low yield, by the following method based on unpublished work by Mr. P. H. Gore. Ethyl oxalate (29·6 g.), followed by *cyclo*heptanone (22·4 g.), was added to a solution of sodium ethoxide (from Na, 4·6 g.) in absolute ethanol (46 ml.) at 5°. Most of the ethanol was removed under reduced pressure, benzene (100 ml.) was added, followed by *n*-propyl bromide (36 ml.) and the mixture was then heated under reflux for 36 hr. After washing with water and removal of benzene, the residue was warmed with aqueous sodium

hydroxide (5%; 200 ml.). Ether-extraction gave a mixture, b. p. 70—100°/16 mm., which on treatment with Brady's reagent afforded a small yield of 2-*n*-propyl*cyclo*heptanone 2 : 4-dinitrophenylhydrazone, m. p. 90°, undepressed on admixture with the specimen obtained as under (*a*).

1-cyclo*Hept*-1′-*enylbut*-2-*en*-1-*ol* (XII; $n = 1$) *and* -*butan*-1-*ol*.—Crotonaldehyde (35 g.) in ether (50 ml.) was added dropwise to a stirred ethereal solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.). Stirring was continued for 12 hr. at room temperature, and saturated aqueous ammonium chloride solution (500 ml.) was then added. The products were worked up as described above, giving 1-cyclo*hept*-1′-*enylbut*-2-*en*-1-*ol* (50 g., 60%), b. p. 72°/0·5 mm., n_D^{21} 1·5010 (Found: C, 79·4; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). Light absorption in EtOH: $\varepsilon < 800$ between 2200 and 3000 Å.

Hydrogenation of the above alcohol (8·7 g.) in ethanol (60 ml.) in the presence of platinic oxide (uptake, 2400 ml. at 18°/762 mm. Calc., 2500 ml.) gave 1-cyclo*heptylbutan*-1-*ol*, b. p. 130°/25 mm., n_D^{23} 1·4776 (Found: C, 77·4; H, 12·6. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%). The 3 : 5-*dinitrobenzoate*, after repeated crystallisation from light petroleum (b. p. 60—80°) and methanol, formed fine needles, m. p. 68° (Found: C, 59·4; H, 6·9; N, 7·5. $C_{18}H_{24}O_6N_2$ requires C, 59·3; H, 6·6; N, 7·7%).

4-cyclo*Hept*-1′-*enylbut*-3-*en*-2-*ol* (XIII; $n = 1$).—The but-2-en-1-ol (XII; $n = 1$) (7 g.) was dissolved in 0·1M-solution of hydrogen chloride in 60% aqueous acetone (200 ml.). After 24 hr. at room temperature, the solution was neutralised with potassium carbonate and worked up in the manner described above, giving 4-cyclo*hept*-1′-*enylbut*-3-*en*-2-*ol* (6 g.), b. p. 87°/0·2 mm., n_D^{20} 1·5293 (Found: C, 79·7; H, 11·0. $C_{11}H_{18}O$ requires C, 79·5; H, 10·9%). Light absorption: see Table.

4-cyclo*Hept*-1′-*enylbut*-3-*en*-2-*one* (XIV; $n = 1$).—The above but-3-enol (2 g.), vacuum-dried manganese dioxide (20 g.), and light petroleum (b. p. 40—60°; 200 ml.) were shaken under nitrogen for 30 hr. at room temperature. After filtration, the solution and washings were fractionated, giving the diene ketone (1·8 g.), b. p. 70°/0·1 mm., n_D^{22} 1·5421. Light absorption: see Table. [Heilbron *et al.*, *J.*, 1949, 1827, give b. p. 76°/0·1 mm., n_D^{24} 1·5400, $\lambda_{max.}$ 2820 Å (ε 16,500).] The ketone formed, in 80% yield, a 2 : 4-dinitrophenylhydrazone which was chromatographed on alumina in benzene–chloroform and crystallised once from ethyl acetate to give red needles, m. p. 187°. After further crystallisation, the m. p. rose to 195° (Found: N, 16·2. Calc. for $C_{17}H_{20}O_4N_4$: N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3060 and 4000 Å, ε 17,000 and 31,000 respectively. The m. p.s of both samples were undepressed on admixture with the authentic specimen, m. p. 188° (*idem*, *ibid.*).

The 2 : 4-dinitrophenylhydrazone was also formed, though only in 10% yield, on direct treatment of 4-*cyclo*hept-1′-enylbut-3-en-2-ol with Brady's reagent (cf. Braude and Forbes, *J.*, 1951, 1762).

1-cyclo*Hept*-1′-*enylhexa*-2 : 4-*dien*-1-*ol* (XII; $n = 2$).—Freshly prepared sorbaldehyde (41 g.; Kuhn and Hoffer, *Ber.*, 1930, **63**, 2168) in ether (60 ml.) was added dropwise to a stirred ethereal solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.) at 0°. Stirring was continued for 3 hr. at room temperature and excess of saturated aqueous ammonium chloride was then added. Working up as described above gave the *dienol* (53 g., 55%), b. p. 90°/5 × 10^{-3} mm., n_D^{20} 1·5285 (Found: C, 80·8; H, 10·5. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). Light absorption in EtOH: $\lambda_{max.}$ 2280 Å, ε 14,500.

6-cyclo*Hept*-1′-*enylhexa*-3 : 5-*dien*-2-*ol* (XIII; $n = 2$).—The above dienol (3 g.) was dissolved in a 0·001M-solution of hydrogen chloride in 60% aqueous acetone (150 ml.). After 12 hr. at room temperature, the solution was neutralised with potassium carbonate and worked up as described above, giving the *dienol* (2 g.), b. p. 92°/5 × 10^{-3} mm., n_D^{20} 1·5835 (Found: C, 80·2; H, 10·1. $C_{13}H_{20}O$ requires C, 81·2; H, 10·5%). Light absorption: see Table.

On treatment of the dienol (1 g.) with Brady's reagent as described for 2-benzylidene*cyclo*heptanol, 6-cyclo*hept*-1′-*enylhexa*-3 : 5-*dien*-2-*one* 2 : 4-*dinitrophenylhydrazone* (0·3 g., 15%) was precipitated. After chromatography on alumina in benzene–chloroform, it crystallised from ethyl acetate in dark red prisms, m. p. 230—232° (decomp.) (Found: N, 15·0. $C_{19}H_{22}O_4N_4$ requires N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3050 and 4030 Å, ε 16,000 and 30,000, respectively.

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456. *Polycyclic Systems. Part V.* A New Route to Azulenes.*

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A new, general route to hydroazulenes and azulenes is described (cf. *Nature*, 1951, **168**, 874). The synthesis of the parent compound starts with *cyclo*heptanone which is converted *via cyclo*heptenyl-lithium into 1-*cyclo*hept-1′-enylallyl alcohol (I; R = H). This is oxidised with manganese dioxide to the corresponding ketone (II; R = H) which is cyclised with formic and phosphoric acids to the octahydroketoazulene (III; R = H). Reduction of the keto-group with lithium aluminium hydride to the alcohol (IV; R = H), followed by dehydration, gives the hexahydroazulene (V; R = H), which is dehydrogenated to azulene (VI; R = H). 1-Methylazulene (VI; R = Me) and 1 : 2-benzazulene (XVI) have been synthesised in analogous ways. Each of the six steps leading to the azulene precursors (V) and (XV) afford yields of 60% or better, but the yields in the last step are poor, as in other methods.

Attempts to prepare precursors of the unknown non-benzenoid hydrocarbons pentalene and heptalene by similar procedures were unsuccessful.

Since the first total synthesis of azulene was achieved by Plattner and Pfau over fifteen years ago (*Helv. Chim. Acta*, 1937, **20**, 224), a considerable variety of synthetic routes to azulene and azulene derivatives have been devised (for reviews, see Pommer, *Angew. Chem.*, 1950, **62**, 281; Gordon, *Chem. Reviews*, 1952, **50**, 127). These methods, however, do not readily lend themselves to the preparation of azulenes on more than a small scale and this is no doubt the main reason why the reactions of this interesting non-benzenoid aromatic system have so far been comparatively little investigated.

The new route described here was suggested by the work reported in Part III (*loc. cit.*; cf. Baddeley, Taylor, and Pickles, *J.*, 1953, 124) on the formation of hydroindanones and hydrofluorenones by the cyclisation of alkenyl *cyclo*hexenyl ketones, now readily accessible by the use of lithium alkenyls. The extension of this approach to the *cyclo*heptenyl analogues provides a convenient method of preparing azulene precursors and is illustrated below by the synthesis of azulene, 1-methylazulene, and 1 : 2-benzazulene. In each case, the immediate azulene precursor, a hexahydroazulene, is obtained from *cyclo*heptanone in six steps, all affording yields of 60% or better and, up to this point, the new route appears to offer advantages over others. In common with earlier methods, however, the last step consists of a catalytic dehydrogenation in which the yield is low. The most promising way of overcoming this difficulty would appear to be the preparation of more highly unsaturated precursors, *i.e.*, tetrahydro- or dihydro-azulenes which may be expected to be dehydrogenated more readily. Work on these lines is in progress in these laboratories.

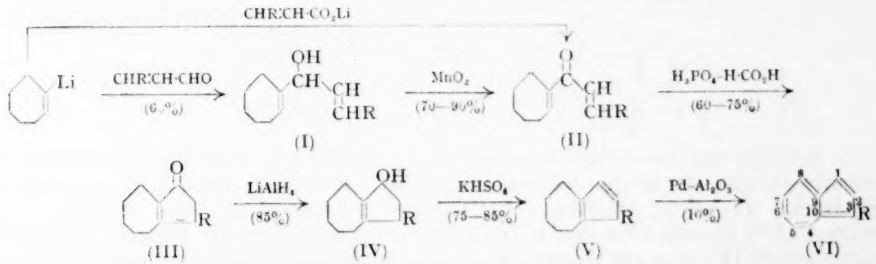
Some unsuccessful attempts to apply procedures similar to those developed for the synthesis of hexahydroazulenes to the preparation of pentalene and heptalene precursors are also recorded.

Synthesis of Azulene and 1-Methylazulene.—The conversion of *cyclo*heptanone into *cyclo*heptenyl-lithium, and the reactions of the latter with acraldehyde and crotonaldehyde to give the alcohols (I; R = H and Me) have already been described (Braude and Forbes, preceding paper). Oxidation with manganese dioxide in light petroleum suspension then gave excellent yields of the ketones (II; R = H and Me), characterised by their 2 : 4-dinitrophenylhydrazones. It has recently been found (Braude and E. A. Evans, to be published) that an alternative and, in some respects, more convenient method of oxidation consists in the use of the chromic oxide–pyridine reagent recently described by Sarett and his co-workers (*J. Amer. Chem. Soc.*, 1952, **74**, 4974; 1953, **75**, 422). The ketone (II; R = Me) was also prepared more directly, though in lower yield, by reaction of *cyclo*heptenyl-lithium with lithium crotonate (cf. Braude and Coles, *J.*, 1950, 2012).

Treatment of the dialkenyl ketones with a mixture of phosphoric and formic acids at 90° (Nazarov and Pinkina, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. chim.*, 1946, 633; 1947, 205;

* Part III, *J.*, 1952, 1430. A paper by Braude and Fawcett, *J.*, 1952, 1528, is regarded as Part IV.

Nazarov, *Uspekhi Khim.*, 1948, **18**, 377; Part III, *loc. cit.*) gave the octahydro-1-keto-azulenes (III; R = H and Me), the structures of which follow from their ultra-violet light absorptions (see Table) and by analogy with their tetrahydroindanone analogues (Part III, *loc. cit.*). The cyclic ketones were characterised by their 2 : 4-dinitrophenylhydrazones, and the lower homologue (III; R = H) also furnished a semicarbazone of m. p. 238°, in good agreement with the values recorded by Plattner and Büchi (*Helv. Chim. Acta*, 1946, **29**, 1608) and Cook, Philip, and Somerville (*J.*, 1948, 164) who prepared the ketone by different routes.



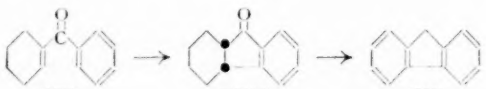
Reduction of the ketones (III) with lithium aluminium hydride afforded the octahydrohydroxyazulenes (IV), characterised by their 3 : 5-dinitrobenzoates; direct cyclisation of the alcohols (I) is not possible because under acid conditions they preferentially undergo anionotropic rearrangement to the conjugated isomers (Braude and Forbes, *loc. cit.*). Dehydration of (IV) with potassium hydrogen sulphate or phthalic anhydride gave the dienes (V), the constitutions of which are confirmed by their ultra-violet light absorptions (see Table), typical of *cyclo*pentadienes. The physical properties of the higher homologue (V; R = Me) were in good agreement with those recorded by Plattner and Büchi (*loc. cit.*).

The final dehydrogenation of the dienes (V) to azulene and 1-methylazulene (VI; R = H and Me) was effected catalytically; the best results were obtained with palladium supported on alumina (cf. Anderson and Nelson, *J. Amer. Chem. Soc.*, 1951, **73**, 232), but the yields did not exceed 10%. This accords with the experience of other investigators, who reported yields of the same order even when highly elaborate techniques were employed (Gordon, *loc. cit.*; Günthard, Süess, Marti, Fürst, and Plattner, *Helv. Chim. Acta*, 1951, **34**, 959). Azulene was purified through the *s*-trinitrobenzene adduct and identified by its melting point and light absorption. 1-Methylazulene (which is a liquid at room temperature) was similarly purified, and was identified by its light absorption and by the mixed melting point of the *s*-trinitrobenzene adduct with a sample kindly provided by Professor Pl. A. Plattner.

Synthesis of 1 : 2-*Benzazulene.*—The extension of the route just described to the synthesis of 4 : 5- or 5 : 6-benzazulenes by starting with the appropriate benzosuberone involves no new principles, but the simplest analogous synthesis of 1 : 2-benzazulene requires the cyclisation of *cyclo*heptenyl phenyl ketone (XI). Since the cyclisation of substituted phenyl vinyl ketones, as distinct from that of substituted divinyl ketones, has previously been accomplished only under rather drastic conditions (cf. Mayer and Müller, *Ber.*, 1927, **60**, 2278), some experiments in corresponding six-membered ring series were carried out first. *cyclo*Hexenyl phenyl ketone (VII) was readily obtained from the alcohol (Braude and Coles, *J.*, 1950, 2014) by oxidation with manganese dioxide and on treatment with phosphoric and formic acids under the conditions used previously, it was smoothly converted into the hexahydrofluorenone (VIII) which was a liquid at room temperature and was characterised by a 2 : 4-dinitrophenylhydrazone, m. p. 158°. This hexahydrofluorenone is different from that of m. p. 42°, obtained by Cook and Hewett (*J.*, 1936, 62) by the Friedel–Crafts cyclisation of 2-phenylhexahydrobenzoic acid and now characterised by a 2 : 4-dinitrophenylhydrazone, m. p. 190°, prepared directly from the semicarbazone.*

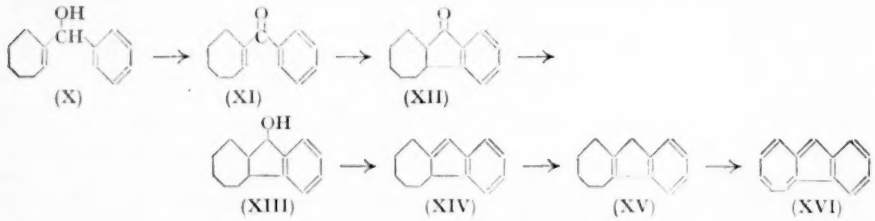
* We are indebted to Professor J. W. Cook, F.R.S., for drawing our attention to this point and for providing a generous sample of the semicarbazone.

The two ketones are, in all probability, stereoisomers; the ketone obtained here would be expected, by analogy with earlier work (Braude and Coles, *loc. cit.*), to have a *cis*-fusion of the two alicyclic rings, whereas Cook and Hewett's ketone would be expected to have a *trans*-fusion, since the 1-phenyl*cyclo*hexanecarboxylic acid from which it was prepared was made by the reduction of *o*-phenylbenzoic acid with sodium and amyl alcohol. Catalytic dehydrogenation of (VIII) with palladium–charcoal at 330° gave fluorene, dehydrogenation being accompanied by reduction of the keto-group as observed in the case of decahydrofluorenone (Part III, *loc. cit.*).



(VII) (VIII) (IX)

No difficulty was experienced in carrying out analogous reactions with the *cyclo*heptene derivatives to give the octahydroketoazulene (XII). Reduction of the latter, followed by dehydration as before, afforded a hexahydro-1 : 2-benzazulene; this may have the structure (XV) (in which the double bond has moved away from the bridgehead position) rather than (XIV) since the location of the ultra-violet absorption maximum corresponds more closely to that expected for a 2 : 3- than a 1 : 2-dialkylated indene (see Table). Dehydrogenation with palladium–alumina gave 1 : 2-benzazulene (XVI) which was identified by its melting point and that of its *s*-trinitrobenzene adduct, and by its light absorption, all in good agreement with the values previously recorded (Plattner, Fürst, Chopin, and Winteler, *Helv. Chim. Acta*, 1948, **31**, 501; Nunn and Rapson, *J.*, 1949, 825).

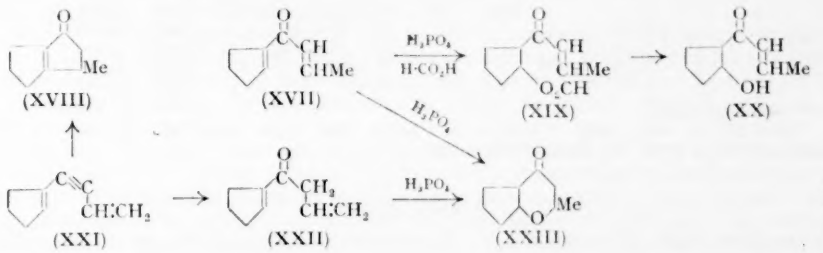


(X) (XI) (XII)

(XIII) (XIV) (XV) (XVI)

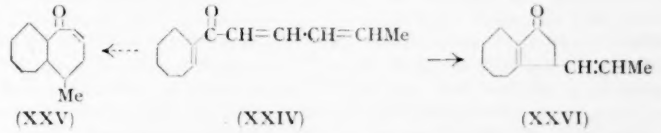
Attempted Syntheses of Pentalene and Heptalene Precursors.—Much interest has been shown in recent years in the possible " aromatic " properties of the unknown pentalene and heptalene, which resemble azulene in containing two fused odd-membered rings, and we attempted to apply procedures similar to those described above to the synthesis of suitable precursors. It was hoped to obtain the hexahydroketopentalene (XVIII) by the cyclisation of the ketone (XVII) prepared by oxidation of the corresponding alcohol (Braude and Forbes, *J.*, 1951, 1755). However, treatment of the ketone (XVII) with a mixture of phosphoric and formic acids gave instead a formate, probably (XIX), together with some of the corresponding alcohol (XX). The formate is evidently produced by the addition of formic acid to the *cyclo*pentenyl group, and the alcohol by subsequent hydrolysis. The addition of formic, as well as other, acids to *cyclo*alkenes has been observed in other cases (cf. Tilichenko, *J. Gen. Chem. Russia*, 1950, **20**, 2152; Morin and Bearse, *Ind. Eng. Chem.*, 1951, **43**, 1596); it appears to occur particularly readily in the *cyclo*pentenyl series (cf. Bergmann and Japhe, *J. Amer. Chem. Soc.*, 1947, **69**, 1826). The formate was characterised by a semicarbazone, and the alcohol by a 2 : 4-dinitrophenylhydrazone; the ester is easily hydrolysed under acid conditions and also gives the derivative of the alcohol on treatment with Brady's reagent. Both the formate and the alcohol, as well as their derivatives, exhibit ultra-violet light absorption characteristic of the presence of an $\alpha\beta$-ethylenic ketone system. When the cyclisation of the ketone (XVII) was attempted with phosphoric acid alone at room temperature, the product was isomeric

with the alcohol (XX) but showed no intense absorption in the 2400-Å region and evolved little methane with methylmagnesium iodide in ether. This appears to be the tetrahydropyrone (XXIII), previously obtained by Nazarov and Burmistrova (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, **1947**, 51) by the treatment of allyl *cyclo*pentenyl ketone (XXII) with phosphoric acid; it gives a semicarbazone which shows ultra-violet absorption ($\lambda_{max.}$ 2250 Å) corresponding to the derivative of a saturated ketone. It is surprising that the Russian authors were apparently able to obtain the desired bicyclic ketone (XVIII) by the direct treatment of 4-*cyclo*pent-1′-enylbut-3-yn-1-ene (XXI) with phosphoric acid, since the cyclisation of the acetylenic hydrocarbon would be expected to proceed by way of the allyl ketone (XXII).



In the meantime, other routes to unsaturated pentalene precursors have been developed and it has been shown that their conversion into pentalene cannot be effected by present methods (Blood and Linstead, *J.*, 1952, 2255; Roberts and Gorham, *J. Amer. Chem. Soc.*, 1952, **74**, 2278; Vogel, *Ber.*, 1952, **85**, 25); for this reason, the present approach was not pursued.

The envisaged approach to the heptalene ring system involved cyclisation of *cyclo*heptenyl pentadienyl ketone (XXIV), a vinylogue of (II), to (XXV), although it was realised that the alternate mode of cyclisation with the formation of a five-membered ring to give (XXVI) was more likely. Treatment of (XXIV) with phosphoric acid in the cold gave mainly unchanged material, but treatment with phosphoric and formic acids at 90° gave a cyclised product which was characterised by a 2 : 4-dinitrophenylhydrazone and exhibited ultra-violet light absorption (see Table) compatible with the structure (XXV); the location of the main maximum (2510 Å) is that expected for a dienone system C:C·CO·C:C (as in II) rather than an enone system C:C·C:O (as in III). Nevertheless the cyclised product must be the hydroazulene derivative (XXVI) and not the hydroheptalene derivative (XXV), for ozonisation gave a quantitative yield of acetaldehyde, showing the presence of a propenyl group.



Light Absorption Properties.—Ultra-violet light absorption data for the various compounds described are collected in the Table. The spectral properties of the conjugated unsaturated ketones of the *cyclo*heptenyl and *cyclo*pentenyl series are very similar to those of the *cyclo*hexenyl series. On the other hand, the maxima of the di-alicyclic unsaturated ketones lie at markedly longer wave-lengths in the hydroazulene than in the hydroindanone series. A particularly marked bathochromic displacement occurs in the propenyl derivative (XXVI); this is presumably due to interaction between the unconjugated propenyl group and the enone system (cf. Braude, *J.*, 1949, 1902). The absorption of the dicyclic dienes (V) is similar to that of *cyclo*pentadiene, but displaced to longer wave-lengths by *ca.* 80 Å, as expected from the presence of two alkyl substituents.

Ultra-violet light absorption (ethanol solutions).

Acyclic ketones.

	$\lambda_{max.}$ Å	ε	$\lambda_{max.}$ Å	ε
(II; R = H)	2510	9,000	*	*
	2580			
(II; R = Me)	2510	12,500	3280	80
*cyclo*Hexenyl propenyl ketone [1]	2570	14,500	3280	80
(XVII)	2510	10,000	3230	75
	2570			
(VII)	2470	12,000	*	*
(XI)	2490	11,500	2800	1900
			3280	120
(XXIV)	2810	9,500	—	—
	2910			
	3020	8,500	—	—

Hydroindanones and hydroketoazulenes.

	$\lambda_{max.}$ Å	ε	$\lambda_{max.}$ Å	ε
(III; R = H)	2410	12,500	2910	85
(III; R = Me)	2440	9,500	3000	70
(XXVI)	2470	9,500	*	*
	2510	10,000	—	—
Tetrahydroindanone [1]	2370	12,500	3020	50
(VIII)	2480	12,300	2800	1300
(XII)	2480	9,600	2800	2400

Cyclic dienes and indenes.

*cyclo*Pentadiene [2]	2390	3,400	—	—
(V; R = H)	2470	4,500	—	—
(V; R = Me)	2460	3,500	—	—
3-Methylindene [3]	2530	8,000	—	—
(XV)	2580	11,000	—	—
	2650	12,000	—	—

* Not determined.

[1] Part III, *J.*, 1952, 1430. [2] Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608. [3] Ramart-Lucas and Hoch, *Bull. Soc. chim.*, 1938, **5**, 848.

Experimental

Ultra-violet light absorptions were determined photographically on a Hilger-Spekker instrument and are only quoted when not included in the Table above. The light absorptions of azulenes in the visible region were determined photoelectrically on a Unicam SP 500 instrument. All 2 : 4-dinitrophenylhydrazones were chromatographed on alumina in benzene–chloroform before crystallisation.

Azulene

cyclo*Hept*-1-*enyl Vinyl Ketone* (II; R = H).—A solution of 1-*cyclo*hept-1′-enylallyl alcohol (13 g.; Braude and Forbes, preceding paper) in light petroleum (b. p. 40—60°; 1300 ml.; sodium-dried) was vigorously shaken with active manganese dioxide (130 g.; vacuum-dried) under nitrogen for 2 days. After filtration and washing of the manganese dioxide with more petroleum, the combined filtrates were concentrated under reduced pressure and fractionated, giving cyclo*hept*-1-*enyl vinyl ketone* (9 g., 70%), b. p. 61°/0·5 mm., n_D^{21} 1·5138 (Found: C, 80·4; H, 9·7. $C_{10}H_{14}O$ requires C, 80·0; H, 9·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in fine red needles, m. p. 198° (Found: C, 58·3; H, 5·7; N, 16·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3860 Å, ε 29,000.

Δ^9-*Octahydro*-1-*ketoazulene* (III; R = H).—The above ketone (12 g.) was added cautiously to an ice-cold mixture of phosphoric acid (90%; 5 g.) and formic acid (98%; 13·5 g.). The addition is exothermic and the mixture gradually darkens. After being allowed to attain room temperature overnight, the solution was kept at 90° for 6 hr., then cooled, diluted with ice-water (200 ml.), and extracted with ether. The ethereal extracts were washed with sodium carbonate solution and with water, dried (Na_2SO_4) and fractionated, giving Δ^9-octahydro-1-ketoazulene (7·2 g., 60%) as a colourless liquid, b. p. 80°/0·8 mm., n_D^{21} 1·5237 (Cook *et al.*, *J.*, 1948, 164, give b. p. 58—60°/0·1 mm., $n_D^{11·5}$ 1·5275). The semicarbazone crystallised from methanol in plates, m. p. 238° (Cook *et al.*, *loc. cit.*, give m. p. 235—236°; Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608, give m. p. 238°). Light absorption in EtOH: $\lambda_{max.}$ 2640 Å, ε 23,200; $\lambda_{infl.}$ 2580 and 2700 Å., ε = 21,700. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red prisms, m. p. 226° (Found: C, 58·2; H, 5·6; N, 16·7. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3960 Å, ε 29,500.

Attempted Cyclisation of 1-cyclo*Hept*-1′-*enylallyl Alcohol* [with E. A. Evans].—The alcohol (6 g.) was dissolved in a mixture of phosphoric acid (3 g.) and formic acid (7 g.) at 0° and then kept first at room temperature and then at 80° for 1 hr. under nitrogen. Dilution with water and isolation of the products with ether as above gave a mixture (4 g.) which showed $\lambda_{max.}$ 2370 Å ($E^{1\%}_{1\,cm.}$ 900) and 2700 Å ($E^{1\%}_{1\,cm.}$ 450) and consisted mainly of 2-allylidene*cyclo*heptanol (Braude and Forbes, *loc. cit.*) and, probably, 2-allylidene*cyclo*heptene. Oxidation of the products with manganese dioxide as above afforded 2-allylidene*cyclo*heptanone which gave no

colour with Schiff's reagent and formed a 2 : 4-*dinitrophenylhydrazone* (dark red needles from ethyl acetate), m. p. 196°, $\lambda_{max.}$ 3000 Å (ε 13,000) and 3980 Å (ε 30,000) in $CHCl_3$ (Found: N, 17·0. $C_{16}H_{18}O_4N_4$ requires N, 17·0%). This derivative appears to be a stereoisomer of the 2 : 4-dinitrophenylhydrazone, m. p. 158°, described previously; it gave a marked m. p. depression on admixture with the derivative, m. p. 198°, of *cyclo*heptenyl vinyl ketone.

Δ^9-*Octahydro*-1-*hydroxyazulene* (IV; R = H).—Lithium aluminium hydride (7 g.) in ether (300 ml.) was slowly added to a stirred solution of the above octahydroketoazulene (10 g.) in ether (40 ml.) at 0°. After 30 min., excess of 2N-sulphuric acid was added, and the ethereal layer was separated, washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and fractionated, giving the *alcohol* (8·5 g., 85%), b. p. 64°/0·1 mm., n_D^{20} 1·5132 (Found: C, 79·1; H, 10·9. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%). The 3 : 5-*dinitrobenzoate* crystallised from ethanol in needles, m. p. 164° (Found: C, 59·0; H, 5·2; N, 8·3. $C_{17}H_{18}O_6N_2$ requires C, 59·0; H, 5·2; N, 8·1%).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydroazulene* (V; R = H).—A mixture of the above octahydrohydroxyazulene (6 g.) and finely powdered potassium hydrogen sulphate (0·6 g.) was rapidly distilled at *ca.* 100° (bath)/*ca.* 0·5 mm. Refractionation of the product gave 1 : 4 : 5 : 6 : 7 : 8-*hexahydroazulene* (4 g., 75%), b. p. 56°/0·5 mm., n_D^{21} 1·5129 (Found: C, 89·5; H, 10·8. $C_{10}H_{14}$ requires C, 89·5; H, 10·5%).

Azulene (VI; R = H).—The final dehydrogenation was carried out in an apparatus similar to that described by Nunn and Rapson (*J.*, 1949, 825) but simplified by omission of the gas-burette, and replacement of the three-way tap by a two-way capillary tap carrying a small cylindrical funnel. The rate of flow of liquid into the catalyst chamber could be controlled quite satisfactorily merely by adjustment of the tap. The catalyst chamber was packed with 1% palladium–alumina and asbestos wool, and the copper heating block was maintained at 320° by means of a Bunsen burner. The hexahydroazulene was passed through the apparatus, evacuated to *ca.* 20 mm., at a rate of *ca.* 1 g./hr. The deep blue products which collected in the receiver were treated with a boiling solution of *s*-trinitrobenzene in ethanol. On cooling, the azulene–trinitrobenzene adduct separated in 3—8% yield; it formed brown needles, m. p. 163°, on recrystallisation from ethanol (Plattner and Pfau, *Helv. Chim. Acta*, 1937, **20**, 224, give m. p. 167°). On passage of a solution of the adduct in hexane through alumina, azulene was regenerated and crystallised in blue needles, m. p. 93° (Plattner and Pfau, *loc. cit.*, give m. p. 99°). A solution of the hydrocarbon in *n*-hexane showed light absorption maxima at 5320, 5565, 5800, 6040, 6330, 6600, and 6980 Å (Plattner and Heilbronner, *Helv. Chim. Acta*, 1947, **30**, 910, give 5410, 5580, 5800, 6030, 6320, 6610, and 6970 Å).

The attempted liquid-phase dehydrogenation of hexahydroazulene, as described below for the 1-methyl homologue, gave only negligible yields of azulene.

1-*Methylazulene*

cyclo*Hept*-1-*enyl Propenyl Ketone* (II; R = Me).—(*a*) A solution of 1-*cyclo*hept-1′-enylbut-2-en-1-ol (5·6 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 500 ml.) was shaken with active manganese dioxide (60 g.) under nitrogen for 3 days. The product was worked up as above, giving cyclo*hept*-1-*enyl propenyl ketone* (5 g., 90%), b. p. 84°/0·4 mm., n_D^{23} 1·5166 (Found: C, 80·6; H, 10·1. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol in red needles, m. p. 118° (Found: C, 59·5; H, 6·1; N, 16·0. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·9; N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 26,500. A small quantity of a second form of the hydrazone, m. p. 129°, was also obtained; it showed identical ultra-violet light absorption.

(*b*) A solution of *cyclo*heptenyl-lithium (from Li, 6·9 g.; Braude and Forbes, *loc. cit.*) in ether (1 l.) was slowly added to a stirred suspension of anhydrous lithium crotonate (45 g.) in ether (100 ml.). After 24 hr. at room temperature, the mixture was cooled in methanol–carbon dioxide, and saturated aqueous ammonium chloride (500 ml.) was added. The ethereal layer was separated, dried (Na_2SO_4), and fractionated, giving *cyclo*heptenyl propenyl ketone (10 g., 14%), b. p. 87°/0·5 mm., identified by the 2 : 4-dinitrophenylhydrazone, m. p. 117°, undepressed on admixture with the specimen described above. The yield could probably be raised considerably by adjusting the conditions.

In another experiment, the formation of *cyclo*heptenyl-lithium from 1-chloro*cyclo*heptene and lithium was allowed to proceed in the presence of lithium crotonate. The consumption of the metal was incomplete, however, and working up as above gave only a 10% yield of ketone, together with much unchanged 1-chloro*cyclo*heptene.

Δ^9-*Octahydro*-1-*keto*-3-*methylazulene* (III; R = Me).—*cyclo*Heptenyl propenyl ketone (6 g.) was treated with a mixture of phosphoric (2·5 g.) and formic (6·5 g.) acids as described above for the lower homologue. Isolation of the product as before gave Δ^9-*octahydro*-1-*keto*-3-*methylazulene* (4·5 g., 75%) as a colourless liquid, b. p. 77°/0·4 mm., n_D^{23} 1·5118 (Found : C, 80·4; H, 9·8. $C_{11}H_{16}O$ requires C, 80·4; H, 9·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in red needles, m. p. 236° (Found : C, 59·5; H, 6·1; N, 16·0. $C_{17}H_{20}O_4N_4$ requires C, 59·3; H, 5·9; N, 16·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3940 Å, ε 26,000.

Δ^9-*Octahydro*-1-*hydroxy*-3-*methylazulene* (IV; R = Me).—The above ketone (3 g.) was reduced with lithium aluminium hydride (1·5 g.) in ether (80 ml.) at 0°. Isolation of the product as before afforded Δ^9-*octahydro*-1-*hydroxy*-3-*methylazulene* (2·5 g., 83%), b. p. 80°/0·4 mm., $n_D^{21\cdot5}$ 1·5058 (Found : C, 79·5; H, 10·9. $C_{11}H_{18}O$ requires C, 79·5; H, 10·8%). Light absorption in EtOH : $\varepsilon < 200$ in the region 2200—4000 Å. The 3 : 5-*dinitrobenzoate* crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 87° (Found : C, 60·0; H, 5·7; N, 7·9. $C_{18}H_{20}O_6N_2$ requires C, 60·0; H, 5·6; N, 7·8%).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydro*-1-*methylazulene* (V; R = Me).—A mixture of Δ^9-octahydro-1-hydroxy-3-methylazulene (8 g.) and potassium hydrogen sulphate (1 g.) was rapidly distilled at *ca.* 0·5 mm. Fractionation of the product gave the hydrocarbon (6 g., 84%), b. p. 66°/0·5 mm., $n_D^{19\cdot5}$ 1·5124 (Plattner and Büchi, *Helv. Chim. Acta*, 1946, **29**, 1608, give b. p. 91—94°/13 mm.).

1-*Methylazulene* (VI; R = Me).—Hexahydro-1-methylazulene (1 g.) and 10% palladium–charcoal (1 g.; Linstead and Thomas, *J.*, 1940, 1130) were placed in a small glass bulb attached to the bottom end of a 30-cm. upright " Pyrex " glass tube, and the bulb was immersed in Wood's metal at 320—340°. A stream of nitrogen was passed through the bulb by means of a capillary tube. The mixture rapidly became dark blue and no further deepening was noticeable after 2 hr. After cooling, the products were extracted with boiling ethanol, and *s*-trinitrobenzene was added. On cooling, the 1-methylazulene–trinitrobenzene adduct (100—150 mg.) crystallised in nearly black prisms, m. p. 155°, undepressed on admixture with Plattner and Büchi's sample (m. p. 154°) (*Helv. Chim. Acta*, 1946, **29**, 1608). Chromatography of the adduct on alumina in hexane regenerated 1-methylazulene as a deep blue liquid. A solution in hexane exhibited light absorption maxima at 5860, 6070, 6330, and 6650 Å (Plattner and Heilbronner, *loc. cit.*, give 5860, 6080, 6350, and 6640 Å).

1 : 2-*Benzazulene*

cyclo*Heptenyl Phenyl Ketone* (XI).—A solution of α-*cyclo*hept-1′-enylbenzyl alcohol (40 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 2 l.) was shaken with active manganese dioxide (180 g.) for 4 days under nitrogen. Isolation of the products as previously gave cyclo*hept*-1-*enyl phenyl ketone* (25 g., 60%), b. p. 95°/5 × 10^{-4} mm., n_D^{22} 1·5591 (Found : C, 83·7; H, 8·4. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone*, which was precipitated only on prolonged warming with Brady's reagent, crystallised from ethyl acetate–methanol in red prisms, m. p. 133—134° (Found : C, 63·1; H, 5·5; N, 15·0. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 31,000.

Octahydro-3-*keto*-1 : 2-*benzazulene* (XII).—*cyclo*Heptenyl phenyl ketone (18 g.) was treated with phosphoric (5 g.) and formic (20 g.) acids, under the conditions previously described. Fractionation of the products afforded *octahydro*-3-*keto*-1 : 2-*benzazulene* (14 g., 75%), b. p. 102°/3 × 10^{-3} mm., n_D^{25} 1·5668 (Found : C, 84·1; H, 8·3. $C_{14}H_{16}O$ requires C, 84·0; H, 8·1%). The 2 : 4-*dinitrophenylhydrazone* was precipitated slowly on treatment with Brady's reagent and crystallised from ethyl acetate in fine red needles, m. p. 206° (Found : C, 63·0; H, 5·4; N, 14·2. $C_{20}H_{20}O_4N_4$ requires C, 63·1; H, 5·3; N, 14·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 26,000.

Octahydro-3-*hydroxy*-1 : 2-*benzazulene* (XIII).—Octahydro-3-keto-1 : 2-benzazulene (14 g.) in dry ether (80 ml.) was cooled to 0° and lithium aluminium hydride (3 g.) in ether was slowly added. Stirring was continued for a further 30 min. and excess of dilute sulphuric acid was then added. The ethereal layer was separated, washed with aqueous sodium carbonate and water, and dried (Na_2SO_4). Removal of the solvent under reduced pressure gave solid *octahydro*-3-*hydroxy*-1 : 2-*benzazulene* (12 g., 85%), which crystallised from light petroleum (b. p. 40—60°) in colourless, monoclinic prisms, m. p. 121° (Found : C, 82·9; H, 9·0. $C_{14}H_{18}O$ requires C, 83·1; H, 9·0%). Light absorption in EtOH : $\lambda_{max.}$ 2650 (ε 750) and 2710 Å (ε 900).

1 : 4 : 5 : 6 : 7 : 8-*Hexahydro*-1 : 2-*benzazulene* (XV).—Octahydro-3-hydroxy-1 : 2-benzazulene (3 g.) and finely powdered potassium hydrogen sulphate (0·3 g.) were thoroughly mixed and rapidly distilled at 100—150° (bath)/10^{-3} mm. Fractionation of the product afforded the

hexahydro-1 : 2-*benzazulene* (2·5 g., 90%) as a colourless liquid, b. p. 86°/10^{-3} mm., n_D^{21} 1·5801 (Found : C, 91·1; H, 8·9. $C_{14}H_{16}$ requires C, 91·25; H, 8·75%).

1 : 2-*Benzazulene* (XVI).—Hexahydro-1 : 2-benzazulene was passed over palladium–alumina at 320—340°/20 mm. at a rate of *ca.* 1 g./hr. in the apparatus described above. The deep blue products were taken up in light petroleum (A) (b. p. 40—60°) and extracted with 90% phosphoric acid at 0°. The deep yellow acid solution was washed with light petroleum and diluted with ice-water. The aqueous solution was extracted with ether, and the ethereal layer was washed with aqueous sodium carbonate and water, dried (Na_2SO_4), and evaporated, giving green plates of 1 : 2-benzazulene, m. p. 170°, in 3—6% yield (Plattner, Fürst, Chopin, and Winteler, *Helv. Chim. Acta*, 1948, **31**, 501, give m. p. 176°). A solution in *n*-hexane exhibited absorption maxima at 5160, 5650, 6150, 6600, 6820, and 7900 Å. The *s*-trinitrobenzene adduct crystallised from ethanol in brown-black needles, m. p. 153° (Plattner *et al.*, *loc. cit.*, give m. p. 155°). Evaporation of the petroleum solution (A) gave largely unchanged hexahydro-1 : 2-benzazulene which could be re-cycled.

1 ; 2-Benzazulene was also obtained in similar yield on passing octahydro-3-hydroxyazulene over palladium–alumina under identical conditions. On the other hand, attempts to effect the dehydration and dehydrogenation in one step by heating with iodine (cf. Treibs, *Annalen*, 1952, **576**, 110) were unsuccessful.

Fluorene

cyclo*Hexenyl Phenyl Ketone* (VII).—A solution of α-*cyclo*hex-1′-enylbenzyl alcohol (2 g.; Braude and Coles, *J.*, 1950, 2014) in light petroleum (b. p. 40—60°; 200 ml.) was shaken with active manganese dioxide (20 g.) for 3 days under nitrogen. Isolation of the product as previously described gave cyclo*hexenyl phenyl ketone* (1·5 g., 75%) as a colourless liquid, b. p. 86°/5 × 10^{-4} mm., n_D^{23} 1·5660, which solidified and crystallised from *n*-pentane in prisms, m. p. 38° (Found : C, 84·1; H, 7·6. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The 2 : 4-*dinitrophenylhydrazone*, which was precipitated only on prolonged warming with Brady's reagent, crystallised from ethyl acetate in orange plates, m. p. 168° (Found : C, 62·4; H, 5·1; N, 15·5. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3870 Å, ε 28,000.

1 : 2 : 3 : 4 : 10 : 11-*Hexahydrofluorenone* (VIII).—*cyclo*Hexenyl phenyl ketone (1 g.) was treated with phosphoric (2 g.) and formic (7 g.) acids under the conditions described previously. Isolation and fractionation of the products gave 1 : 2 : 3 : 4 : (cis ?)10 : 11-*hexahydrofluorenone* (0·8 g., 80%) as a colourless liquid, b. p. 86°/2 × 10^{-3} mm., n_D^{25} 1·5631 (Found : C, 83·5; H, 7·8. $C_{13}H_{14}O$ requires C, 83·8; H, 7·6%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate–methanol in orange-red plates, m. p. 158° (Found : C, 62·0; H, 5·0; N, 15·3. $C_{19}H_{18}O_4N_4$ requires C, 62·3; H, 5·0; N, 15·3%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 30,000.

Treatment of the hexahydrofluorenone semicarbazone, m. p. 212°, described by Cook and Hewett (*J.*, 1936, 71), with 2 : 4-dinitrophenylhydrazine in ethanol–sulphuric acid gave 1 : 2 : 3 : 4 : (trans ?)10 : 11-*hexahydrofluorenone* 2 : 4-*dinitrophenylhydrazone* which crystallised from ethyl acetate in needles, m. p. 190—191° (Found : C, 61·9; H, 4·8; N, 15·6%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3910 Å, ε 28,000.

Fluorene (IX).—A mixture of hexahydrofluorenone (1 g.) and 25% palladium–charcoal (0·1 g.) was heated at 300° in a stream of nitrogen for 20 hr. The crude product did not give a precipitate with Brady's reagent. Extraction with boiling light petroleum (b. p. 60—80°) gave fluorene (0·4 g.) which after one recrystallisation had m. p. 110°, undepressed on admixture with an authentic specimen.

Attempted Syntheses of Pentalene and Heptalene Precursors

cyclo*Pent*-1-*enyl Propenyl Ketone* (XVII).—A solution of 1-*cyclo*pent-1′-enylbut-2-en-1-ol (30 g.; Braude and Forbes, *J.*, 1951, 1755) in light petroleum (b. p. 40—60°; 2 l.) was shaken with active manganese dioxide (230 g.) for 3 days under nitrogen. Isolation of the product in the usual manner gave cyclo*pent*-1-*enyl propenyl ketone* (18 g., 60%) as a colourless liquid, b. p. 66°/0·6 mm., n_D^{21} 1·5137, which solidified at 0° and crystallised from pentane in plates, m. p. 34° (Found : C, 78·9; H, 8·6. $C_9H_{12}O$ requires C, 79·35; H, 8·9%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red needles, m. p. 152° (Found : N, 17·6. $C_{15}H_{16}O_4N_4$ requires N, 17·7%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3900 Å, ε 28,000.

Attempted Cyclisation of cyclo*Pentenyl Propenyl Ketone*.—(*a*) The foregoing ketone (16 g.) was treated with phosphoric (7·5 g.) and formic acid (20 g.) for 6 hr. at 90°. Isolation of the

products as previously described and fractionation afforded (i) 2-*hydroxy*cyclo*pentyl propenyl ketone* (XX) (7 g.), b. p. 40°/0·1 mm., n_D^{20} 1·4912, $\lambda_{max.}$ (in EtOH) 2310 and 3240 Å, ε 8000 and 50 (Found: C, 70·7; H, 8·8%; active H, 0·8 atom. $C_9H_{14}O_2$ requires C, 70·1; H, 9·15%), and (ii) the corresponding *formate* (XIX) (3 g.), b. p. 73°/0·1 mm., n_D^{20} 1·4840, which solidified and after crystallisation from pentane had m. p. 30°, $\lambda_{max.}$ (in EtOH) 2400 and 3100 Å, ε 10,000 and 40, $\lambda_{infl.}$ 3200 Å, ε 30 (Found: C, 65·9; H, 7·8. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·75%). The *semicarbazone* of the formate separated from methanol in fine colourless needles, m. p. 158° (Found: C, 55·1; H, 7·5; N, 18·1. $C_{11}H_{17}O_3N_3$ requires C, 55·2; H, 7·2; N, 17·6%). Light absorption in EtOH: Max. at 2570 Å (ε 23,500), inflections at 2510 and 2660 Å (ε 16,000 and 20,000). The hydroxy-ketone was also obtained when the formate was heated with 2N-hydrochloric acid in 60% ethanol at 80° for 30 min. On treatment of either the hydroxy-ketone or the formate with Brady's reagent, the 2 : 4-*dinitrophenylhydrazone* of the hydroxy-ketone was obtained; it crystallised from methanol in fine red needles, m. p. 191° (Found: C, 54·0; H, 5·4; N, 16·6. $C_{15}H_{18}O_5N_4$ requires C, 53·8; H, 5·3; N, 16·7%). Light absorption in $CHCl_3$: Max. at 3880 Å, ε 26,000.

(*b*) Treatment of *cyclo*pentenyl propenyl ketone (3 g.) with phosphoric acid (15 g.) at room temperature for 15 hr. and isolation of the products as before gave the pyrone (XXIII) as a colourless liquid, b. p. 62°/0·1 mm., n_D^{24} 1·4861, ε < 1000 between 2200 and 3000 Å (Found: C, 70·5; H, 9·3. Calc. for $C_9H_{14}O_2$: C, 70·1; H, 9·15%) (Nazarov and Burmistrova, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1947, 51, give b. p. 72—73°/4 mm., n_D^{20} 1·4802). With methylmagnesium iodide in ether, it evolved methane corresponding to 0·3 active hydrogen atom. The semicarbazone crystallised from ethanol in prisms, m. p. 182° (Found: N, 20·5. Calc. for $C_{10}H_{17}O_2N_3$: N, 19·9%) (Nazarov and Burmistrova give m. p. 181°). Light absorption in EtOH: Max. at 2280 Å, ε 11,000.

cyclo*Hept*-1-*enyl Pentadienyl Ketone* (XXIV).—A solution of 1-*cyclo*hept-1′-enylpenta-2 : 4-dien-1-ol (20 g.; Braude and Forbes, *loc. cit.*) in light petroleum (b. p. 40—60°; 2 l.) and active manganese dioxide (200 g.) were vigorously agitated for 36 hr. under nitrogen. Isolation of the product in the usual way and fractionation afforded the *ketone* (15 g., 75%) as a pale yellow liquid, b. p. 114°/4 × 10^{-4} mm., n_D^{17} 1·5413 (Found: C, 82·3; H, 10·0. $C_{13}H_{18}O$ requires C, 82·1; H, 9·55%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red prisms, m. p. 219—222° (decomp.) (Found: C, 61·1; H, 6·1; N, 15·0. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 6·0; N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 4030 Å, ε 33,000.

Δ^9-*Octahydro*-1-*keto*-3-*propenylazulene* (XXVI).—The above ketone (9 g.) was treated with phosphoric acid (7·5 g.) and formic acid (20·1 g.) under the conditions previously described. Isolation of the product as before and fractionation gave mainly Δ^9-*octahydro*-1-*keto*-3-*propenylazulene* (2·2 g., 24%), b. p. 67°/5 × 10^{-4} mm., n_D^{20} 1·5290 (Found: C, 81·8; H, 9·85. $C_{13}H_{18}O$ requires C, 82·1; H, 9·55%). The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark-red, rectangular prisms, m. p. 212° (decomp.) (Found: C, 61·8; H, 6·25; N, 15·1. $C_{19}H_{22}O_4N_4$ requires C, 61·6; H, 6·0; N, 15·1%). Light absorption in $CHCl_3$: $\lambda_{max.}$ 3930 Å, ε 31,500.

Ozone was passed through a solution of the ketone (0·8 g.) in acetic acid (10 g.) for 2 hr. (until the absorption had ceased). The resulting solution was steam-distilled and the distillate collected in a receiver containing Brady's reagent, giving acetaldehyde 2 : 4-dinitrophenylhydrazone (0·9 g., 90%) which on recrystallisation from ethyl acetate separated as red needles, m. p. 165°, undepressed on admixture with an authentic specimen.

Attempts to effect the cyclisation of (XXIV) by treatment with phosphoric acid alone at 0° only gave small yields of the octahydroazulene (XXVI), most of the starting material being recovered unchanged.

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457. *Effect of Alkyl Substitution on Absorption Spectra.*

By H. C. Barany and M. Pianka.

The hypsochromic shifts observed in the absorption spectra of azines containing alkyl substituents on the carbon atoms of the azomethine groups, and in those of the thia- and selena-carbocyanines with an alkyl substituent on the *meso*-carbon atom, as well as the bathochromic shifts in the absorption spectra of 2 : 4-dinitrophenylhydrazones of aliphatic aldehydes, may be due to the hyperconjugative effect of the alkyl group. The effect of alkyl groups on the absorption maxima of the above-mentioned 2 : 4-dinitrophenylhydrazones and thia- and selena-carbocyanines is found to be comparable with the effect of alkyl groups in the *p*-position on the hydrolysis of diphenylmethyl chloride.

Azines substituted with an alkyl group in the azomethine chain, and thia- and selena-carbocyanines with an alkyl substituent on the *meso*-carbon atom, exhibit hypsochromic shifts with respect to their parent compounds. These shifts cannot be due to the steric

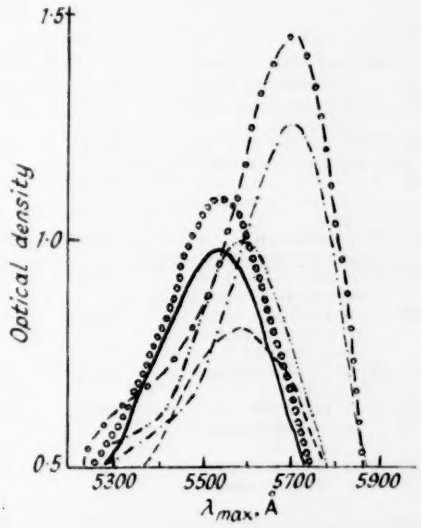


Fig. 1. *Absorption spectra of carbocyanines (in methanol).*

— · — · — 3 : 3′-Diethylselenacarbocyanine iodide.
———— 3 : 3′-Diethyl-9-methylselenacarbocyanine iodide.
— — — — 3 : 3′ : 9-Triethylselenacarbocyanine iodide.
— o — o — 3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine iodide.
oooooooo 3 : 3′-Diethyl-5 : 6 : 5′ : 6′ : 9-pentamethylthiacarbocyanine iodide.
— ·· — ·· — 3 : 3′ : 9-Triethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine iodide.

effect, since in both the azines and the cyanines the bulkier ethyl group causes a smaller hypsochromic shift than the methyl group (Tables 1 and 2; absorption spectra of some carbocyanines in methanol are given in Fig. 1). Moreover, for thia- and selena-carbocyanines it was shown that there is no shift of absorption if the ethyl group is replaced by *n*-propyl, *n*-butyl, or amyl groups (Brooker and White, *J. Amer. Chem. Soc.*, 1935, **57**, 547).

The replacement of an ethylenic by an azomethine group in azines and carbocyanines causes a hypsochromic shift in their absorption maxima. In azines this shift corresponds to an increase in the excitation energy by about 3 kcal./mole (Barany, Braude, and Pianka, *J.*, 1949, 1898), which may be due to impedance of the flow of π-electronic energy along the conjugated system by the high electronic density on the nitrogen atoms of the azomethine groups. Thus replacement of $CH\!:$ by $N\!:$ brings about resistance to complete conjugation. In azines, alkyl substituents attached to the carbon atoms of the azomethine groups may exert a hyperconjugative effect (Pianka, Thesis, London, 1950, pp. 85—89; Szmant and Planinsek, *J. Amer. Chem. Soc.*, 1950, **72**, 4983), thereby increasing the electron density on the nitrogen atoms. This may yet further impede the π-electron flow along the con-

jugated system, thus causing still greater hypsochromic shifts (Table 1; only principal absorption bands are given).

TABLE 1.

	$\lambda_{max.}$, Å	ε	$\Delta\lambda_{max.}$, Å *	$\Delta\lambda_{max.}$, Å †
1 : 4-Diphenylbutadiene	3280	41,000 [1]	—	
Benzylideneazine	3000	28,000 [2]	−280	—
Methyl phenyl ketazine	2670	24,500 [2]		−330
Ethyl phenyl ketazine	2700	20,500 [3]		−300
1 : 8-Diphenyloctatetraene	3750	90,000 [1]	—	
Cinnamylideneazine	3500	65,000 [2]	−250	—
Methyl styryl ketazine	3220	45,100		−280
1-Naphthylmethyleneazine	3540	30,000 [3]		—
Methyl 1-naphthyl ketazine	2930	18,000 [3]		−610
2-Naphthylmethyleneazine	3300	69,000 [2]		—
Methyl 2-naphthyl ketazine	2620	48,000 [3]		−680

* Effect of replacing CH·CH by N·N. † Effect of alkyl substitution.
[1] Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384. [2] Barany, Braude, and Pianka, *loc. cit.* [3] Blout, Eager, and Gofstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1986.

TABLE 2.

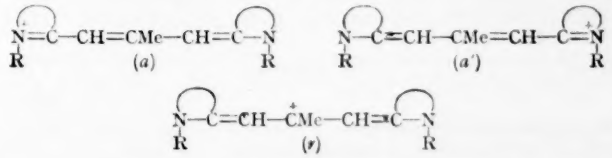
	No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\lambda_{max.}$, Å, 9-Et substituted dye	$\Delta\lambda'_{max.}$, Å, 9H to 9Me	$\Delta\lambda''_{max.}$, Å, 9H to 9Et	$\Delta\lambda''_{max.}/\Delta\lambda'_{max.}$
(C1)	3 : 3′-Diethylthiacarbocyanine	5575 [1]	5430 [1]	5475 [1]	−145	−100	0·69
(C2)	3 : 3′-Diethyl-6 : 6′-dimethylthiacarbocyanine	5620	5475	5525	−145	− 95	0·66
(C3)	3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethylthiacarbocyanine	5700	5530	5580	−170	−120	0·70
(C4)	3 : 3′-Diethyl-6 : 7 : 6′ : 7′-dibenzothiacarbocyanine	5940 [2]	5700 [2]	5740 [2]	−240	−200	0·83
(C5)	3 : 3′-Diethyl-4 : 5 : 4′ : 5′-dibenzothiacarbocyanine	5950 [1]	5750 [1]	5785 [1]	−200	−165	0·83
(C6)	3 : 3′-Diethyl-4 : 5 : 4′ : 5′-tetraphenylthiazolocarbocyanine	5890	5600	5670	−290	−220	0·76
(C7)	3 : 3′-Diethylselenacarbocyanine	5675 [1, 3]	5525 [1]	5575 [2]	−150	−100	0·67
(C8)	3 : 3′-Diethyl-5 : 5′-dimethoxyselenacarbocyanine	5890	5670		−220		
C9)	3 : 3′-Diethyl-6-methyl-4′ : 5′-benzothiacarbocyanine	5800	5510	5635	−290	−165	0·57
(C10)	3 : 3′-Diethyl-5-methoxyselena-4′ : 5′-benzothiacarbocyanine	5920	5675	5720	−245	−200	0·82

[1] Brooker and White, *loc. cit.* [2] *Idem, ibid.*, p. 2480. [3] Clark *J.*, 1933, 216.

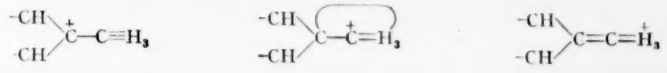
Moffitt (*Proc. Phys. Soc.*, 1950, **63**, *A*, 700) considered the following structures as the most important contributors to the total resonance of the formamidinium ion : (*a*) $\dot{N}R_2{:}CH{\cdot}NR_2$; (*a'*) $NR_2{\cdot}CH{:}\overset{+}{N}R_2$; (*r*) $NR_2{\cdot}\overset{+}{C}H{\cdot}NR_2$. Of these, *a* and *a'* may be combined to give combinations a^+, a^- of both symmetries; *r* is essentially of the completely symmetric + species. The ground state of the formamidinium ion and its higher vinylogues is completely symmetric. The first excited state is, however, anti-symmetric with respect to a reflection in the plane of symmetry (*i.e.*, perpendicular to the molecular plane). Structures which are essentially symmetric can therefore only contribute to the ground state. Hence structure *r* contributes to the stabilisation of the ground state only.

The hypsochromic effect of *meso*-alkyl substituents in thia- and selena-carbocyanines (as shown in Table 2) can therefore be explained. In the absence of any hyperconjugative

effect, the energetic relation of the three most important contributors to the resonance of the system, *viz.*,



is, of course, the same as if the substitution had not been effected. However, by the co-operation of the hyperconjugative effect the positive charge may migrate out of the main conjugation path. (This movement of the positive charge in cationic systems is critical, other effects being of only secondary importance; therefore, basically the same considerations will apply to carbocyanines with two different heterocyclic nuclei.) The charge can move only through the medium of structure *r* as follows:



(In the case of higher alkyl substituents, second- instead of first-order hyperconjugation is operative. This is reflected in a less pronounced hypsochromic shift.) Since these structures are completely symmetric, they have the effect of stabilising structure *r*, which can thus participate more fully in the resonance which stabilises the ground state with respect to the excited state. The nearer *r* and *a*,*a*′ approach each other in energy, the greater the stabilisation. Accordingly, the transition from the ground state to the first excited state is hypsochromically affected.

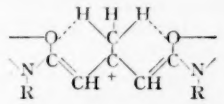
The oxacarbocyanines differ from the thia- and selena-carbocyanines in that they show bathochromic shifts when substituted in the *meso*-position by alkyl groups, which exert a weighting effect of 30—60 Å per methylene group (Table 3) (Pianka and Barany, *J.*, 1948, 309).

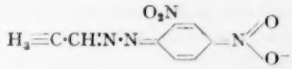
TABLE 3.

	No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\Delta\lambda_{max.}$, Å, 9H to 9Me
(C11)	3 : 3′-Diethyloxacarbocyanine	4825 [a]	4885 [a]	+60
(C12)	3 : 3′-Diethyl-5 : 5′-diphenyloxacarbocyanine	4940	5000	+60
(C13)	3 : 3′-Diethyl-5 : 6 : 5′ : 6′-tetramethyloxacarbocyanine	4955	5010	+55

[a] Brooker and White, *loc. cit.*, p. 551.

Koch (*J.*, 1951, 514) postulated hydrogen bonding between the carbonyl and the methyl group in *O*-methyltropolone to account for its having essentially the same C=O frequency (1615 cm.$^{-1}$) as in tropolone (1620 cm.$^{-1}$). Similar hydrogen bonding may occur in oxacarbocyanines, leading to the formation of six-membered rings involving the hydrogen atoms of the alkyl groups and the oxygen atoms of the heterocycle as in (I). (Short, *J.*,

(I) 

 (II)

1952, 4587, found that hydrogen bonding occurs not only with semipolar, but also with covalent, oxygen atoms, as with those of dioxan.) This hydrogen bonding would exclude the movement of the positive charge out from the main conjugation path in the manner and by the mechanism suggested for structure *r*. There would be therefore no contribution from type *r* to the ground state, and consequently no stabilisation of the ground state with respect to the excited state.

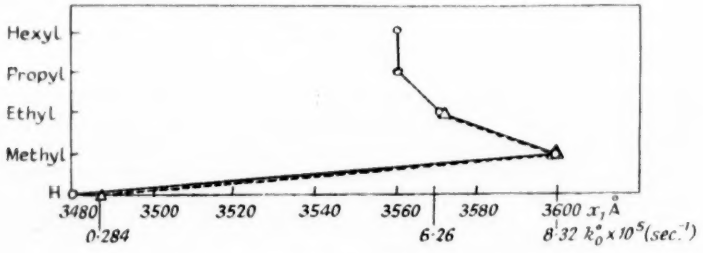
In oxathia- and oxaselena-carbocyanines there is the possibility of hydrogen bonding between the oxygen atom of the oxazole and the *meso*-alkyl group which would weaken the latter's hyperconjugative effect. This may be responsible for the less pronounced hypsochromic shift (Table 4) than in thia- and selena-carbocyanines. The effect of terminal

TABLE 4.

	No. and name of dye (iodides)	$\lambda_{max.}$, Å	$\lambda_{max.}$, Å, 9-Me substituted dye	$\Delta\lambda_{max.}$, Å, 9H to 9Me
(C14)	3 : 3′-Diethyl-5′ : 6′-dimethyl-5-phenyloxathiacarbocyanine	5300	5260 *	−40
(C15)	3 : 3′-Diethyl-5′-methoxy-5-phenyloxaselenacarbocyanine	5405	5340	−65

* Isolated as perchlorate.

FIG. 2. *Curves obtained on plotting the absorption maxima of* 2 : 4*-dinitrophenylhydrazones of aliphatic aldehydes* (*Table* 5) (————) *and the kinetic constants at* 0° *of the hydrolysis of the diphenylmethyl derivatives* (*Table* 6) (– – – – –) *against the ascending homologous series.*



alkyl groups is visible in Table 5, showing the absorption maxima of 2 : 4-dinitrophenylhydrazones of a homologous series of aliphatic aldehydes (results of Braude and Jones, *J.*, 1945, 499; only principal bands are quoted).

TABLE 5.

[R = 2 : 4-$(NO_2)_2C_6H_3$·]

	$\lambda_{max.}$, Å	$+\Delta\lambda_{max.}$, Å		$\lambda_{max.}$, Å	$+\Delta\lambda_{max.}$, Å
H·CH:N·NHR	3480	—	Pr·CH:N·NHR	3560	80
Me·CH:N·NHR ...	3600	120	Hexyl·CH:N·NHR...	3560	80
Et·CH:N·NHR	3570	90			

In so far as there is a bathochromic shift of 120 Å from the first to the second member of the series, and of only 80 Å between successive higher homologues, there cannot be a weighting effect, since this causes a bathochromic shift of 30—60 Å per CH_2 group (Pianka and Barany, *loc. cit.*). These shifts can be attributed to the hyperconjugative effect which is most pronounced in the acetaldehyde derivative through production of forms such as (II) by first-order hyperconjugation. A similar ratio (0·75 ± 0·09) is found among thia- and selena-carbocyanines between the hypsochromic shifts of dyes substituted in the *meso*-position with an ethyl and those substituted with a methyl group (last col. of Table 2; the ratio does not hold, however, for dye No. 9). This ratio of 0·75 also obtains for the kinetic constants governing the hydrolysis of alkyl-substituted diphenylmethyl chlorides (Table 6 and Fig. 2).

TABLE 6.[a, b]

p-R·C_6H_4·CHPhCl	$k_{25} \times 10^3$ (sec.$^{-1}$)	$+\Delta k$	$k_0 \times 10^5$ (sec.$^{-1}$)	$+\Delta k$	$E_{act.}$ (kcal.)	ΔE
R = H	0·072	—	0·284	—	20·9	—
R = Me	1·559	1·487	8·32	8·036	18·9	−2·0
R = Et	1·260	1·188	6·26	5·976	19·4	−1·5

[a] Hughes, Ingold, and Taher *J.*, 1940, 949. [b] Arnold, Murai, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 4193.

Experimental

Key to Symbols used in Tables, etc.—Bases according to the following references: (B 1) 2 : 6-Dimethylbenzothiazole (Jacobson, *Ber.*, 1889, **22**, 907), (B 2)* 2 : 5 : 6-trimethylbenzothiazole, (B 3) 2-methyl-4 : 5-diphenylthiazole (Hubacher, *Annalen*, 1890, **259**, 244), (B 4)* 5-methoxy-2-methylbenzoselenazole, (B 5)* 2-methyl-5-phenylbenzoxazole, (B 6) 2 : 5 : 6-trimethylbenzoxazole (Diepolder, *Ber.*, 1911, **44**, 2499), (B 7) 2-methyl-β-naphthathiazole (Hamer, *J.*, 1929, 2589).

Quaternary agents. (QA 1) Diethyl sulphate, (QA 2) ethyl iodide, (QA 3) ethyl toluene-*p*-sulphonate.

Orthoesters and anilides. (R 1) Ethyl orthoformate, (R 2) ethyl orthoacetate, (R 3) ethyl orthopropionate, (R 4) ethyl *N*-phenylthiolacetimidate, (R 5) ethyl *N*-phenylthiolpropionimidate, (R 6) trianilinomethane.

Quaternary salts. (QS 1) 3-Ethyl-2 : 6-dimethylbenzothiazolium ethyl sulphate, (QS 2) 3-ethyl-2 : 6-dimethylbenzothiazolium iodide, (QS 3) 3-ethyl-2 : 5 : 6-trimethylbenzothiazolium iodide, (QS 4) 3-ethyl-2-methyl-4 : 5-diphenylthiazolium ethyl sulphate, (QS 5) 3-ethyl-5-methoxy-2-methylbenzoselenazolium iodide, (QS 6) 2-(2-acetanilidovinyl)-3-ethyl-6-methylbenzothiazolium iodide, (QS 7) 2-2′-anilinopropenyl-3-ethyl-6-methylbenzothiazolium iodide, (QS 8) 2-(2-anilinobut-1-enyl)-3-ethyl-6-methylbenzothiazolium iodide, (QS 9) 2-2′-acetanilidovinyl-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 10) 2-2′-anilinopropenyl-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 11) 2-(2-anilinobut-1-enyl)-3-ethyl-5-methoxybenzoselenazolium iodide, (QS 12) 3-ethyl-2-methyl-5-phenylbenzoxazolium toluene-*p*-sulphonate, (QS 13) 3-ethyl-2-methyl-5-phenylbenzoxazolium ethyl sulphate, (QS 14) 3-ethyl-2 : 5 : 6-trimethylbenzoxazolium toluene-*p*-sulphonate, (QS 15) 3-ethyl-2 : 5 : 6-trimethylbenzoxazolium ethyl sulphate, (QS 16) 2-2′-acetanilidovinyl-3-ethyl-5-phenylbenzoxazolium ethyl sulphate, (QS 17) 2-2′-anilinopropenyl-3-ethyl-5-phenylbenzoxazolium ethyl sulphate, (QS 18) 3-ethyl-2-methyl-β-naphthathiazolium toluene-*p*-sulphonate.

3 : 4-*Dimethylphenylthiourea.*—Hydrochloric acid (32%; 52 c.c.) was added during 30—40 min. to 3 : 4-xylidine (64 g.) at 90°. Chlorobenzene (150 c.c.) was added and then, at 60°, dry ammonium thiocyanate (40 g.), after which the mixture was stirred during 5 hr. at 90° and set aside overnight at 10°; the yellow solid which separated was filtered off and washed well with water. Buff needles of the *thiourea*, obtained from ethanol, had m. p. 188° (Found: C, 60·0; H, 6·6; N, 15·4. $C_9H_{12}N_2S$ requires C, 59·9; H, 6·6; N, 15·5%).

2-*Amino*-5 : 6-*dimethylbenzothiazole.*—3 : 4-Dimethylphenylthiourea (33 g.) was suspended in chlorobenzene (150 c.c.; dried by distilling off 10% under reduced pressure). To the well-stirred mixture initially cooled to 5° (ice-bath), sulphuryl chloride (16 c.c.) and a few drops of bromine were added slowly from a dropping-funnel, the mixture being kept at 15—20°; it was then stirred at room temperature for 12 hr. Water (30 c.c.) was added, and the chlorobenzene removed by steam-distillation. The clear solution was filtered from a little solid matter, and cooled, and the base was precipitated by an excess of 15% aqueous sodium hydroxide. After two recrystallisations from methanol (charcoal), the *thiazole* was obtained as a light yellow powder, m. p. 185° (Found: C, 64·1; H, 6·0; N, 16·5. $C_9H_{10}N_2S$ requires C, 64·2; H, 5·9; N, 16·6%).

2-*Acetamido*-4 : 5-*dimethylphenyl Thiolacetate.*—2-Amino-5 : 6-dimethylbenzothiazole (5·4 c.c.), potassium hydroxide (5·8 g.), and water (18 c.c.) were heated in an autoclave for 6 hr. at 210°. The resulting clear brown solution was diluted with water (35 c.c.) and cooled to 0—5°, and a mixture of glacial acetic acid (32 c.c.) and acetic anhydride (32 c.c.) added, the temperature being kept at 5°. The white *thiolacetate* which separated was stirred for 1 hr., filtered off, washed with water, and dried in a vacuum-desiccator; it formed colourless crystals, m. p. 225°, from alcohol (Found: C, 60·7; H, 6·2; N, 5·8. $C_{12}H_{15}O_2NS$ requires C, 60·7; H, 6·3; N, 5·9%).

2 : 5 : 6-*Trimethylbenzothiazole* (B 2).—The foregoing thiolacetate (47·5 g.) was added during 30 min. to a boiling mixture of glacial acetic acid (30 c.c.) and acetic anhydride (45 c.c.), which was then refluxed for 9 hr. during which zinc dust (3 g.) was added in small portions. The cold solution was poured on crushed ice (250 g.), made alkaline with 3N-sodium hydroxide, and extracted with carbon tetrachloride (3 × 100 c.c.). After drying (Na_2SO_4), the solvent was removed, and the *base* distilled at 143°/5 mm., m. p. 83° (from benzene) (Found: C, 67·6; H, 6·3; N, 7·8. $C_{10}H_{11}NS$ requires C, 67·7; H, 6·2; N, 7·9%).

2 : 2′-*Diamino*-4 : 4′-*dimethoxydiphenyl Diselenide.*—2-Nitro-*p*-anisidine (25 g.) was heated

* The preparation of the bases thus marked and of the required intermediates is described in detail.

in concentrated hydrochloric acid (25 c.c.) till dissolved (15 min.) and cooled to 0°; crushed ice (75 g.) was added, and then sodium nitrite (13·4 g.) at 5°. The diazotized solution was made alkaline to Congo-red with sodium acetate. An aqueous solution of potassium selenocyanate (152 c.c.) [prepared by dissolving selenium (129 g.) in a solution of potassium cyanide (112 g.) in water (63 c.c.) at 100° and dilution with water (89 c.c.)] was added during 2 hr., at <10°. The brown precipitate which separated was filtered off and washed with water. This was probably 4-methoxy-2-nitrophenyl selenocyanate, but could not be obtained pure as it decomposed on drying. It was reduced by dissolving it in an aqueous solution of sodium hydroxide (11 g.), adding sodium dithionite (hydrosulphite) (15 g.) in water (60 c.c.) at 65°, and stirring the mixture at 90° for 30 min. When air was bubbled through the cold mixture, the yellow *diselenide* separated. When filtered off, washed well with water, and dried in a desiccator, this formed yellow crystals, m. p. 170° (from ethanol) (Found: N, 6·8. $C_{14}H_{16}O_2N_2Se_2$ requires N, 6·9%).

5-Methoxy-2-methylbenzoselenazole (B 4).—The above diselenide (25 g.) was dissolved in acetic anhydride (140 c.c.) at 70°. The solution was stirred, heated under reflux to boiling, and zinc dust (22 g.) added during 10 hr. with stirring; the mixture was refluxed for a further 15 hr., then cooled, and zinc acetate was filtered off and washed with hot glacial acetic acid (40 c.c.). The filtrate and washings were freed from solvent under reduced pressure (18 mm.), and the residue was extracted with methylene chloride (3 × 50 c.c.). The crude base, which distilled at 150°/10 mm., was dissolved in hydrochloric acid (30%), the solution treated with charcoal and filtered, and the base reprecipitated with dilute ammonia and extracted with methylene chloride. The extract was dried (Na_2SO_4), and the pure *base* distilled as a yellow oil, b. p. 190°/3 mm., m. p. 54° (from methylene chloride) (Found: N, 6·1. C_9H_9ONSe requires N, 6·2%).

2-Methyl-5-phenylbenzoxazole (B 5).—Acetic anhydride (60 c.c.) and 3-amino-4-hydroxydiphenyl (20 g.) (Raiford and Colbert, *J. Amer. Chem. Soc.*, 1925, **47**, 1457) were refluxed for 2 hr., and then distilled under reduced pressure. The *base* distilled as a pale yellow oil at 158°/2—3 mm., m. p. 60—61° (from ethanol) (Found: N, 6·9. $C_{14}H_{11}ON$ requires N, 6·9%).

Details of preparation of quaternary compounds.

	Reactants				Bath-temp.	Reaction time, hr.	M. p.	Formula	Found (%): N	Found (%): I	Reqd. (%): N	Reqd. (%): I
QS 1 *	B 1	3·3 g.	QA 1	3·5 c.c.	120°	0·3	—	—	—	—	—	—
QS 2 [1]	B 1	3·7 g.	QA 2	2·1 c.c.	100 †	48	157—158°	—	—	—	—	—
QS 3	B 2	21 g.	QA 2	12 c.c.	100	18	235	$C_{12}H_{16}NSI$	4·1	37·8	4·2	38·0
QS 4 *	B 3	5 g.	QA 1	2·7 c.c.	160	0·3	—	—	—	—	—	—
QS 5	B 4	22·6 g.	QA 2	9·3 g.	100	48	204 ‡	$C_{11}H_{14}ONSeI$	3·6	33·0	3·7	33·3
QS 12 *	B 5	4·25 g.	QA 3	4 g.	130	0·5	—	—	—	—	—	—
QS 13 *	B 5	6 g.	QA 1	3·3 g.	140—150	0·3	—	—	—	—	—	—
QS 14 *	B 6	10·5 g.	QA 3	10·5 g.	140	4	—	—	—	—	—	—
QS 15 *	B 6	5·6 g.	QA 1	3·3 c.c.	160	0·3	—	—	—	—	—	—
QS 18 *	B 7	33·5 g.	QA 3	33·5 g.	180	5	—	—	—	—	—	—

* Quaternary salts marked with an asterisk were not isolated, but the whole yield was used, after cooling, for the subsequent condensation to dyes, except that QS 18 was triturated with ether–acetone, and the solid used for subsequent condensations. QS 2, QS 3, and QS 5 were purified by grinding them with excess of acetone, filtering, and washing with acetone and then ether, and then recrystallising them from ethanol. All three compounds are crystalline.

† In closed tube. ‡ With decomp. [1] Jacobson, *Ber.*, 1889, **22**, 907.

Details of Dye Syntheses.—With the exception of C 14M which was isolated as the perchlorate, all dyes were isolated as the iodides. Those for which quaternary salts other than iodides were used, were converted into the iodides by pouring the cooled reaction mixtures into excess of 10% aqueous potassium iodide with vigorous stirring. The crude dyes were then allowed to solidify, filtered off, washed with acetone, and twice recrystallised from methanol. For all dye condensations dry pure pyridine was used. The condensations were carried out in boiling-tubes provided with a long air-condenser and immersed in an oil-bath kept between 120° and 140°.

Table 2*a* gives details of syntheses of the dyes listed in Table 2; the last letter in the number of dye signifies that the *meso*-substituent (on $C_{(9)}$) is a hydrogen atom (H), or a methyl (M) or ethyl group (E).

Table 3*a* corresponds to Table 3 and Table 4*a* to Table 4. The convention as regards H, M, and E operates also here.

Methyl Styryl Ketazine.—This, m. p. 166° (from benzene), was prepared from benzylideneacetone and hydrazine sulphate as described by Knoepfer (*Monatsh.*, 1909, **30**, 38).

Details of syntheses of anilinovinyl compounds.

Reactants				Solvents (c.c.) *	Bath-temp.	Reaction time, min.	M. p.	Formula	N, %: Found	N, %: Reqd.
QS 6	QS 2	10·7 g.	R 6 10·7 g.	An (3·6), Ac (3·6)	100°	180	249—250°	$C_{20}H_{21}ON_2SI$	6·2	6·0
QS 7	QS 2	10·6 g.	R 4 6·4 c.c.	---	170	30	230	$C_{19}H_{21}N_2SI$	6·6	6·4
QS 8	QS 2	10·6 g.	R 5 6·9 c.c.	---	170	30	190	$C_{20}H_{23}N_2SI$	6·2	6·2
QS 9	QS 5	7·6 g.	R 6 6·4 g.	An (2·3), Ac (2·3)	100	180	238—239	$C_{20}H_{21}O_2N_2SeI$	5·2	5·3
QS 10	QS 5	12·7 g.	R 4 6·4 c.c.	---	170	30	216	$C_{19}H_{21}ON_2SeI$	5·3	5·6
QS 11	QS 5	12·7 g.	R 5 6·9 c.c.	---	170	30	194	$C_{20}H_{23}ON_2SeI$	5·2	5·5
QS 16	QS 13 from 6 g. of B 5		R 6 9·1 g.	An (3), Ac (3)	100	180	187	$C_{27}H_{28}O_6N_2S$	5·4	5·5
QS 17	QS 13 from 6 g. of B 5		R 4 5·9 c.c.	---	180	180	190	$C_{24}H_{28}O_5N_2S$	5·6	5·8

* An = Acetic anhydride; Ac = glacial acetic acid; --- no solvent.

Purification: After cooling, the anilinovinyl compounds were repeatedly triturated with methanol–ether (1 : 1). The solids which separated were filtered off, washed with ether till the washings were colourless, and recrystallised twice from methanol.

Appearance: QS 6, rust-red plates; QS 7, violet crystals; QS 8, glittering, maroon needles; QS 9, olive-green crystals; QS 10, bluish-grey crystals; QS 11, green powder; QS 16 orange-yellow powder; QS 17 yellow powder.

TABLE 2*a*.

No. of dye	Reactants *				Pyridine (c.c.)	Reaction time, min.	M. p.	Formula	N, %: Found	N, %: Reqd.
C 2H [1]	QS 1 N.I.	R 1	2 c.c.		5	60	275—276°	$C_{23}H_{25}N_2S_2I$	5·47	5·38
C 2M [1, 2]	QS 2 2 g.	R 2	4·6 c.c.		15	45	274	$C_{24}H_{27}N_2S_2I$	5·30	5·21
C 2E [2]	QS 1 N.I.	R 5	2 c.c.		5	150	245—247	$C_{25}H_{29}N_2S_2I$	5·15	5·11
C 3H	QS 3 2·3 g.	R 1	0·76 g.		20	60	265—267	$C_{25}H_{29}N_2S_2I$	4·87	5·11
C 3M	QS 3 2·3 g.	R 2	0·9 g.		20	60	275—276	$C_{26}H_{31}N_2S_2I$	4·86	4·98
C 3E	QS 3 3·3 g.	R 5	1·5 c.c.		5	90	254—255	$C_{27}H_{33}N_2S_2I$	5·09	4·86
C 6H [3]	QS 4 N.I.	R 1	2·3 c.c.		15	90	247—250	$C_{37}H_{33}N_2S_2I$	4·02	4·02
C 6M	QS 4 N.I.	R 2	2·3 c.c.		15	90	253	$C_{38}H_{35}N_2S_2I$	4·05	3·94
C 6E	QS 4 N.I.	R 3	2·3 c.c.		15	90	261	$C_{39}H_{37}N_2S_2I$	3·75	3·87
C 8H	QS 5 3·9 g.	R 1	1·8 c.c.		20	60	267—268	$C_{23}H_{25}O_2N_2Se_2I$	4·49	4·33
C 8M	QS 5 3·9 g.	R 2	1·8 c.c.		20	60	248—249	$C_{24}H_{27}O_2N_2Se_2I$	4·37	4·24
C 9H	QS 6 1·6 g.	QS 18	2·2 g.		15	90	216	$C_{26}H_{25}N_2S_2I$	5·03	5·04
C 9M	QS 7 1·7 g.	QS 18	2·2 g.		15	16 hr.	252—254	$C_{27}H_{27}N_2S_2I$	5·08	4·91
C 9E	QS 8 1·7 g.	QS 18	2·2 g.		15	16 hr.	225	$C_{28}H_{29}N_2S_2I$	4·55	4·79
C 10H	QS 9 4·0 g.	QS 18	4·4 g.		15	60	237—238	$C_{26}H_{25}ON_2SSeI$	4·35	4·52
C 10M	QS 10 2·1 g.	QS 18	2·2 g.		15	60	227—228†	$C_{27}H_{27}ON_2SSeI$	4·30	4·42
C 10E	QS 11 2 g.	QS 18	2 g.		10	150	210—213†	$C_{28}H_{29}ON_2SSeI$	4·40	4·31

* N.I. denotes that the quaternary salt was not isolated, but used *in situ*. The quantities are shown in the Table giving details of preparation of quaternary compounds (p. 2222).

† With decomp.

[1] Kiprianov, Suitnik, and Suich, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 42. [2] U.S.P. 2,378,783/1945. [3] U.S.P. 2,079,376/1939.

Appearance of dyes: C 2H, greenish-black needles; C 2M, mauve crystals; C 2E, greenish-black crystals; C 3H, glittering black needles; C 3M, mauve crystals; C 3E, ink-blue crystals; C 6H, dark purple plates; C 6M, dark green crystals; C 6E, dark violet powder; C 8H, dark green needles; C 8M, dark violet plates with a reddish reflex; C 9H, dark blue crystals; C 9M, purple crystals; C 9E, dark crystals with a violet reflex; C 10H, dark violet crystals with a bluish reflex; C 10M, dark purple plates; C 10E, violet crystals with olive-green reflex.

TABLE 3*a*.

No. of dye	Reactants				Pyridine (c.c.)	Reaction time, min.	M. p.	Formula	N, %: Found	N, %: Reqd.
C 12H	QS 12	N.I.*	R 1	12 c.c.	12	30	240°	$C_{33}H_{39}O_2N_2I$	4·69	4·58
C 12M	QS 13	N.I.	R 4	3·1 c.c.	10	150	273—274	$C_{34}H_{31}O_2N_2I$	4·23	4·47
C 13H	QS 14	N.I.	R 1	6·8 c.c.	32	240	280—281	$C_{25}H_{29}O_2N_2I$	5·50	5·43
C 13M	QS 15	N.I.	R 4	3·1 c.c.	10	150	253—256	$C_{26}H_{31}O_2N_2I$	5·16	5·28

* See footnote * in Table 2A.

Appearance of dyes: C 12H, scarlet needles; C 12M, red powder; C 13H, glittering red long needles; C 13M, red powder.

TABLE 4*a*.

No. of dye	Reactants, g.				Medium * (and c.c.)	Reaction time, min.	M. p.	Formula	N, %: Found	Reqd.
C 14H	QS 16	3·4	QS 3	3·3	Py (20), An (2)	60	270°	$C_{29}H_{39}ON_2SI$	4·53	4·83
C 14M	QS 17	6	QS 3	6	Py (18)	180	250—253	$C_{30}H_{31}O_5N_2SCl$	4·81	4·94
C 15H	QS 16	1·2	QS 5	0·95	Py (3·5), An (3·5)	20	262	$C_{28}H_{27}ON_2SeI$	4·28	4·57
C 15M	QS 17	3·5	QS 5	3·8	Py (20), An (25)	60	247	$C_{29}H_{29}ON_2SeI$	4·33	4·31

* Py = pyridine; An = acetic anhydride.

Appearance of dyes : C 14H, glittering dark green needles; C 14M (precipitated as perchlorate by stirring and forming the crude dye with excess of 10% aqueous potassium perchlorate), plum-red crystals; C 15H, glittering, dark blue needles; C 15M, dark maroon crystals.

Light-absorption Measurements.—Absorptions of the carbocyanines were determined in methanol solution, that of methyl styryl ketazine in ethanol.

We thank the late Dr. H. P. Koch and Dr. W. E. Moffitt for helpful discussions, Mr. J. L. Walpole for the determination of m. p.s of the dyes on a modified Kofler block, and Dr. C. G. Smith for his continued interest.

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458. *The Organic Chemistry of Phosphorus. Part I. Some New Methods for the Preparation of Alkyl Halides.**

By S. R. LANDAUER and H. N. RYDON.

Triphenyl phosphite methiodide has been shown to react with alcohols, thus :

$$(PhO)_3PMeI + ROH \longrightarrow RI + PhOH + Me{\cdot}PO(OPh)_2$$

The reaction gives good yields of alkyl iodides from a wide variety of alcohols; alkyl chlorides can be prepared similarly from triphenyl phosphite benzylochloride, $(PhO)_3P(CH_2Ph)Cl$. Alkyl halides can also be prepared conveniently and in good yield according to the general equation :

$$(PhO)_3P + ROH + XHal \longrightarrow RHal + X{\cdot}PO(OPh)_2 + PhOH$$

where X = alkyl or hydrogen; poor yields are obtained where X = NH_4, Na, or Li. These reactions are of value as new methods for the preparation of alkyl halides; their mechanisms are briefly discussed.

THE work described in this paper had its origin in a general investigation of the influence of structure on the Arbusov reaction (Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687; cf. Michaelis and Kähne, *Ber.*, 1898, **31**, 1048) in which an alkyl halide reacts with a trialkyl phosphite, thus :

$$(RO)_3P + R'Hal \longrightarrow R'{\cdot}PO(OR)_2 + RHal$$

(for a comprehensive review of this reaction see G. M. Kosolapoff, " Organophosphorus Compounds," John Wiley & Sons, New York, 1950, p. 121). If R = R′ the reaction becomes formally catalytic, a small amount of an alkyl halide, RHal, serving to convert a large amount of a trialkyl phosphite, $(RO)_3P$, into the isomeric dialkyl alkylphosphonate, $R{\cdot}PO(OR)_2$. This was realised by the earlier workers (Arbusov, *loc. cit.*; Arbusov and Razumov, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 167) but direct experimental evidence is scanty and we record experiments which show that as little as 0·01 mol. of methyl iodide will bring about the isomerisation of trimethyl phosphite; methyl sulphate is as effective for this purpose as methyl iodide.

The intervention of the " quasi-phosphonium " compound, $(RO)_3PR'Hal$, in the reaction was postulated by Arbusov (*loc. cit.*) and this view has been generally accepted; it is supported by Kosolapoff's finding (*J. Amer. Chem. Soc.*, 1944, **66**, 109) that the curve

* The work described in this paper has been the subject of a preliminary communication (*Chem. and Ind.*, 1951, 313), and of two patent applications (B.P. Appln. 20,639/1950 and 2889/51).

relating the production of RHal to the reaction time is sigmoid and by the not entirely satisfactory kinetic work of Zawidski and Staronka (*Bull. int. Acad. Sci. Cracovie, A*, 1915, 319). In the complete reaction scheme

$$(RO)_3P + R'Hal \longrightarrow (RO)_3PR'Hal \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$
$$(RO)_3PR'Hal \longrightarrow R'\cdot PO(OR)_2 + RHal \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

all the evidence points to the second stage being normally the rate-determining one; thus the action of methyl iodide on triethyl phosphite produces almost exclusively diethyl methylphosphonate, presumably because stage (i) has gone to completion before any appreciable amount of ethyl iodide has been liberated in stage (ii), and it is only when RHal is much more reactive than R'Hal that any competition between the two halides for the available phosphite is observed (*e.g.*, in the reaction between triethyl phosphite and ethylene dibromide; Ford-Moore and Williams, *J.*, 1947, 1465).

In the case of triaryl phosphites both stages of the reaction are slow and it is easy to isolate the intermediate quasi-phosphonium compound (Michaelis and Kähne, *loc. cit.*, Broeker, *J. prakt. Chem.*, 1928, **118**, 287). It seemed important to study the chemistry of these compounds and we accordingly prepared triphenyl phosphite methiodide,* $(PhO)_3PMeI$; by rapid working with exclusion of moisture, we obtained this compound as needles, m. p. 146° (Michaelis and Kähne, *loc. cit.*, give m. p. 70—75°). In an attempt to determine the nature of the phosphorus–iodine bond in this compound, we treated it with alcoholic silver nitrate; precipitation of silver iodide was slow, and not instantaneous as with methyltriphenylphosphonium iodide. In order to exclude the possibility that the time-dependent production of silver iodide was due to reaction of the silver nitrate with methyl iodide formed by dissociation, the compound was treated with cold ethanol and methyl iodide was sought in the product; surprisingly, ethyl iodide was formed, together with phenol and diphenyl methylphosphonate.

This promised a method for the preparation of alkyl iodides and therafter we concerned ourselves mainly with the preparative aspect of the reaction. Triphenyl phosphite methiodide was found to react with a wide variety of alcohols according to the equation:

$$(PhO)_3PMeI + ROH \longrightarrow RI + PhOH + Me\cdot PO(OPh)_2$$

This appears to be quite general.

The preparative procedure is very simple; the alcohol and the methiodide, which need not be purified, are merely mixed in equivalent proportions; cooling may be necessary with the more reactive, and gentle warming with the less reactive, alcohols; the product is worked up either by direct distillation or by washing out the phenol with alkali, followed by distillation or crystallisation. Working on the 0·05—0·1-molar scale the yields of iodide obtained from thirteen alcohols varied from 60 to 95%; no attempt was made to establish optimal conditions and it seems likely that 90% yields will generally be attainable. The method is satisfactory with primary, secondary, and tertiary alcohols, unsaturated alcohols, glycols, and ethyl lactate; conversion of the last-named into ethyl α-iodopropionate in excellent yield makes this useful reagent much more accessible than it has been by the older and less direct methods (Bodroux and Taboury, *Bull. Soc. chim.*, 1907, **1**, 910; Kenyon, Phillips, and Turley, *J.*, 1925, **127**, 414). The direct production, albeit in poor yield, of cholesteryl iodide from cholesterol is of interest since this iodide has previously only been obtained indirectly (Beynon, Heilbron, and Spring, *J.*, 1936, 907; Helferich and Günther, *Ber.*, 1939, **72**, 338; Shoppee and Summers, *J.*, 1952, 1786).

Michaelis and Kähne (*loc. cit.*) also prepared triphenyl phosphite benzylochloride, $(PhO)_3P(CH_2Ph)Cl$, as an uncrystallisable oil, and we have used this substance to prepare *n*-hexyl chloride and 2-chloro-octane in excellent yield from the corresponding alcohols; there is not doubt that this method, too, is general.

Attempts to prepare tribenzyl phosphite methiodide failed owing to its immediate decomposition into benzyl iodide and dibenzyl methylphosphonate.

It is not necessary to isolate the quasi-phosphonium compound and alkyl chlorides,

* We prefer this non-committal name to the systematic alternatives, methyltriphenoxyphosphonium iodide for the electrovalent and triphenyl methylphosphoranoiodidotrioate for the covalent structure.

bromides, and iodides can be readily prepared by merely refluxing together equimolecular quantities of triphenyl phosphite, an alcohol, and an alkyl halide, thus :

$$(PhO)_3P + ROH + R'Hal \longrightarrow RHal + R'\cdot PO(OPh)_2 + PhOH \quad . \quad . \quad . \quad . \quad (iii)$$

It is necessary, in order to avoid competition between R'Hal and RHal for unchanged phosphite, for R'Hal to be more reactive than RHal, unless the latter is removed as fast as it is formed (an example of this procedure is given on p. 2231) ; the most convenient halides for preparative use are benzyl chloride, benzyl bromide, and methyl iodide, although others can be used (examples will be found in the Experimental section). The reactants are best heated together by use of an electric mantle since the temperature can this conveniently be slowly raised as the usually more volatile R'Hal is used up ; if the temperature is not raised during the reaction the yield may be much reduced or the necessary reaction time unduly prolonged ; the progress of the reaction can be followed conveniently by observing the internal temperature of the gently refluxing reaction mixture. A wide variety of alkyl halides has been prepared in this way in yields varying from 60 to 99% ; yields of 90% should be attainable in most cases. In general this method is more convenient than that employing the preformed quasi-phosphonium compound, although the latter may be preferable when the alcohol or iodide is heat-sensitive (*e.g.*, in the preparation of *cyclo*-hexyl and *tert.*-butyl iodides). The new method gives excellent results with sterically hindered alcohols which are difficult to convert into halides by conventional methods ; thus *neo*pentyl iodide was obtained from the alcohol in 74% yield, a great improvement over earlier methods (Whitmore, Whittle, and Harriman, *J. Amer. Chem. Soc.*, 1939, **61**, 1585), and 1 : 3-di-iodo-2 : 2-dimethylpropane in 85% yield from the corresponding glycol (conventional methods fail for this preparation ; the dibromide was obtained in 35% yield by Whitmore, Popkin, Bernstein, and Wilkins, *J. Amer. Chem. Soc.*, 1941, **63**, 124). Other phosphites may replace triphenyl phosphite ; thus *n*-butyl iodide was obtained in 40% yield from triethyl phosphite, butanol, and methyl iodide, but was accompanied by much ethyl iodide produced by the direct Arbusov reaction between triethyl phosphite and methyl iodide.

Equation (iii) can be generalised, thus :

$$(PhO)_3P + ROH + XHal \longrightarrow RHal + X\cdot PO(OPh)_2 + PhOH \quad . \quad . \quad . \quad . \quad (iv)$$

and we report here our results for the cases where X = H, NH_4, Li, and Na ; work is in progress on the case where X = Halogen (cf. B.P. Appln. 20,205/1951) and our results will be reported later. A number of alkyl chlorides, including unsaturated alkyl chlorides, have been prepared in moderate to good yield (45—100%) by passing dry hydrogen chloride into a mixture of an alcohol and triphenyl phosphite. *n*-Butyl halides have also been prepared by heating *n*-butyl alcohol and triphenyl phosphite with ammonium chloride, sodium chloride, lithium bromide, and sodium iodide ; the yields were poor except with ammonium chloride, which gave a 63% yield.

Several plausible mechanisms for the reaction between triphenyl phosphite methiodide and an alcohol can be envisaged, but the evidence available is hardly sufficient to enable a definite conclusion to be reached. Mechanisms which would lead to the intermediate formation of hydrogen iodide seem to be excluded by our finding that dimethylaniline ethiodide, rather than the hydriodide, is produced when triphenyl phosphite methiodide reacts with ethanol in the presence of dimethylaniline. An acceptable mechanism must also accommodate our observation that configurational inversion accompanies the formation of 2-iodo-octane from octan-2-ol ; the very considerable racemisation which accompanies inversion is doubtless due to the prolonged contact of the alkyl iodide with iodide ions (cf. Hughes, Juliusberger, Masterman, Topley, and Weiss, *J.*, 1935, 1527). The mechanism which we adopt as a working hypothesis is the following, in which ester interchange is followed by the second stage of the normal Arbusov reaction :

$$(PhO)_3PMeI + ROH \longrightarrow (PhO)_2(RO)PMeI + PhOH$$

$$(PhO)_2(RO)PMeI \longrightarrow Me\cdot PO(OPh)_2 + RI$$

The great strength of the phosphorus–carbon bond would seem to rule out the possibility that the first stage is composite, involving initial dissociation of the methiodide into its components.

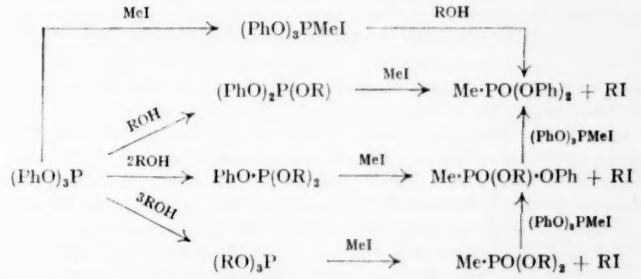
The three-component reaction (equations iii and iv) is demonstrably more complex, ester-interchange playing an important part. Ester-interchange between triphenyl phosphite and many alcohols occurs very readily; thus, the odour of trimethyl phosphite becomes apparent within a few minutes of mixing triphenyl phosphite and methanol at room temperature. Ester-interchange between equimolecular proportions of triphenyl phosphite and *n*-butyl alcohol yields one molecular proportion of phenol together with all the possible phosphites, *viz.*, tri-*n*-butyl phosphite, di-*n*-butyl phenyl phosphite, *n*-butyl diphenyl phosphite, and triphenyl phosphite. The action of methyl iodide on the resulting mixture of phosphites occurs in two stages, the first of which undoubtedly proceeds by the normal Arbusov mechanism but is incapable of giving rise to the high observed yields of alkyl halide. This is followed by a slower liberation of more *n*-butyl iodide which can only be accounted for by reaction between triphenyl phosphite methiodide and butyl methylphosphonates produced in the first stage; the occurrence of such a reaction has been independently established in the case of dimethyl methylphosphonate which reacts readily with triphenyl phosphite methiodide, thus :

$$Me{\cdot}PO(OMe)_2 + 2(PhO)_3PMeI \longrightarrow 2MeI + 3Me{\cdot}PO(OPh)_2$$

Alkyl iodides are also formed by the action of triphenyl phosphite methiodide on trialkyl phosphites, *e.g.* :

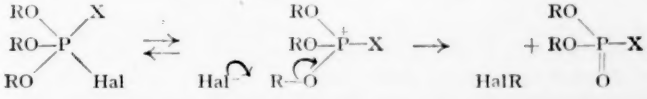
$$(BuO)_3P + (PhO)_3PMeI \longrightarrow BuI + Me{\cdot}PO(OBu)_2 + (PhO)_3P$$

but this reaction is unlikely to be of any importance in the three-component reaction since the Arbusov reaction with alkyl phosphites is much faster than the formation of triphenyl phosphite methiodide. The three-component reaction between triphenyl phosphite, an alcohol and methyl iodide probably involves all the reactions summarised in the following scheme :



the extent to which each participates depending on the reactivity of ROH.

All the reactions involve a stage identical with the second stage of the normal Arbusov reaction. The absence of rearrangement in the formation of the *neo*pentyl halides and the configurational inversion which accompanies the formation of the 2-halogeno-octanes suggest that the process is of this *S*2 type :



The absence of configurational inversion in the formation of the cholesteryl halides is paralleled by the similar anomaly observed with other reagents and is no doubt to be explained in the same way (cf. Shoppee, *J.*, 1946, 1147). The formation of unrearranged *neo*pentyl halides from *neo*pentyl alcohol is of interest in view of the widely held opinion that reactions involving *neo*pentyl–oxygen bond fission are invariably accompanied by rearrangement (cf. Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274); since our experiments were completed, Sommer, Blankman, and Miller (*J. Amer. Chem. Soc.*, 1951, **73**, 3542) have observed similar absence of rearrangement in *S*2 conversions of *neo*pentyl alcohol into *neo*pentyl halides.

An *S*2 mechanism for the second stage of the Arbusov reaction is further supported by experiments with mixed trialkyl phosphites which react with methyl iodide with the

liberation, as alkyl iodide, of the least electron-releasing alkyl group (methyl in preference to ethyl, and ethyl in preference to *iso*propyl); similar observations were also made in the reactions of the same mixed phosphites with water.

Experimental

For all values of α, $l = 1$.

Isomerisation of Trimethyl Phosphite.—(*a*) Trimethyl phosphite (McCombie, Saunders, and Stacey, *J.*, 1945, 380) (0·1 mol.) was refluxed with methyl iodide at 100° for 30 min. After a brief induction period, a vigorous reaction set in and was complete within 5 min. Distillation gave methyl iodide, collected in a trap at −80°, and dimethyl methylphosphonate, b. p. 63°/10 mm. (Found: C, 28·9; H, 7·3. Calc. for $C_3H_9O_3P$: C, 29·1; H, 7·3%). The yields were as follows:

Molar ratio, phosphite : iodide	Methyl iodide formed (%)	Phosphonate formed (%)
1 : 1	92	90
2 : 1	79	88
10 : 1	77	93
100 : 1	—	80

(*b*) Trimethyl phosphite (6·2 g., 0·05 mol.) and methyl sulphate (0·06 g., 0·0005 mol.) were heated under reflux at 100° for 15 min. Visible reaction commenced after 2 min. and was complete after 5 min. Distillation gave trimethyl phosphite (0·5 g., 8%; recovered from trap at −80°) and dimethyl methylphosphonate, b. p. 66°/12 mm. (5·0 g., 81%).

Triphenyl Phosphite Methiodide.—Triphenyl phosphite (31 g.) and methyl iodide (21 g.) were heated (electric mantle) under reflux, with the exclusion of moisture, for 36 hr.; the temperature of the refluxing mixture rose from 70° to 115° during the reaction. Treatment of the product with anhydrous ether gave small yellowish-brown needles of the methiodide which were repeatedly washed with anhydrous ether and finally dried and weighed *in vacuo* (42 g., 94%). Large colourless crystals can be obtained by seeding the mixture after 3 hr. The pure compound is obtained as follows: The crude material is warmed gently with "AnalaR" acetone, and the saturated solution obtained by decantation is rapidly treated with an equal volume of dry ether; the methiodide separates in beautiful flat needles which are collected by centrifugation, washed several times with anhydrous ether, and dried in a vacuum-desiccator (P_2O_5). Two such crystallisations gave pure *triphenyl phosphite methiodide*, m. p. 146° (Found: C, 50·5; H, 4·2; I, 27·2. $C_{19}H_{18}O_3PI$ requires C, 50·45; H, 4·0; I, 28·1%). In the recrystallisation it is essential to minimise the time of contact with acetone and to work rapidly and with rigorous exclusion of moisture. The crude material was used for all the experiments described below; it was stored under ether, and dried and weighed *in vacuo* immediately before use.

Reaction of Triphenyl Phosphite Methiodide with Ethanolic Silver Nitrate.—A solution of the methiodide (7·95 g.) in absolute ethanol (30 ml.) was treated with saturated ethanolic silver nitrate (150 ml.). The precipitated silver iodide was filtered off after 3 min., washed with alcohol and ether, dried, and weighed; further crops were recovered from the filtrate at various times. The total yields of silver iodide were:

Time, mins.	3	6	10	20	80	150	1440
AgI, %	67	73	76	79	86	92	100

In a control experiment, triphenylphosphine methiodide (204·5 mg.) gave 118·3 mg. (99·6%) of silver iodide after 3 min.; no further precipitate was obtained from the filtrate.

Reaction of Triphenyl Phosphite Methiodide with Ethanol.—The methiodide (21 g.) was dissolved in absolute ethanol (35 ml.) by shaking for a few min.; distillation gave fractions (i) b. p. 65—79°/760 mm., (ii) b. p. 45—60°/0·04 mm., and (iii) b. p. 138—140°/0·04 mm. Fraction (i) was diluted with water (3 vols.), and the heavy oil which separated was dried ($CaCl_2$) and distilled; it had b. p. 72° and was identified as ethyl iodide (4·5 g., 62%) by conversion into ethyldimethylphenylammonium iodide, m. p. 136—137°. Fraction (ii) solidified and was completely soluble in sodium hydroxide solution; it was identified as phenol by conversion into 2 : 4 : 6-tribromophenol, m. p. 95—96°. Fraction (iii) was washed twice with 2N-sodium hydroxide and with water; on cooling in ice, diphenyl methylphosphonate (10·5 g., 91%) crystallised (m. p. 35—36°).

In a second experiment, volatile material was distilled off at 0·5 mm. and collected in a trap at −80°. The condensate was refluxed with dimethylaniline (6 g.) and gave ethyldimethylphenylammonium iodide (8·5 g., 66%), m. p. 132—133°. The residue was repeatedly washed

with 2N-sodium hydroxide and water; the insoluble diphenyl methylphosphonate (9·9 g., 86%) solidified on cooling (m. p. 35°); acidification of the alkaline washings gave phenol (4 g., 96%), m. p. 39—40°, characterised as 2 : 4 : 6-tribromophenol, m. p. 93—94°.

Preparation of Alkyl Iodides from Triphenyl Phosphite Methiodide.—The alcohol was cautiously added to the calculated amount of crude triphenyl phosphite methiodide; cooling was necessary with the more reactive, and gentle warming with the less reactive, alcohols. After completion of the reaction, the alkyl iodide was isolated by one of the following procedures :

(A) The iodide was distilled directly from the reaction mixture under reduced pressure and collected in a trap at −80°. The condensate was repeatedly washed with water, dried (minimum quantity of Na_2SO_4 or K_2CO_3), and redistilled. This is the most convenient procedure for iodides with b. p.s substantially below that of phenol.

(B) The iodide and phenol were distilled directly, under reduced pressure, from the reaction mixture. The distillate, alone or admixed with ether, was repeatedly washed with ice-cold dilute sodium hydroxide solution and water, dried, and distilled.

(C) The reaction mixture was taken up in ether, and the phenol removed by repeated washing with dilute sodium hydroxide solution and water; drying and distillation then gave the iodide and diphenyl methylphosphonate.

The results of some experiments, on the 0·05—0·1-molar scale, are summarised in the Table.

Iodide	Conditions	Isolation	Yield (%)	B. p.*	Characterisation
*iso*Propyl	Room temp.	A	75	86—87°	*iso*Propylpyridinium iodide, m. p. 112—113° (decomp.)
n-Butyl	Room temp., 30 min.	A	72	130	n_D^{19} 1·4980; *n*-butylquinolinium iodide, m. p. 174°
sec.-Butyl	Room temp., 2 hr.	A	60	115—120	n_D^{18} 1·4980
tert.-Butyl	50—60°; 1 hr.	A	76 †	(i) 85—95 (ii) 95—100	(i) n_D^{21} 1·4703 (ii) n_D^{21} 1·4885
1-Methylheptyl	Steam-bath 20 hr. Ether (450 ml./mol.) added	A	80	45—50 (0·8)	(Found: I, 52·8. Calc. for $C_8H_{17}I$: I, 52·9%); $\alpha_D^{20\cdot4}$ + 0·1° [from (−)-octan-2-ol, $\alpha_D^{20\cdot4}$ − 7·83°]
,,	80—100°, 1 hr.	A	65	99—100 (8)	$\alpha_D^{22\cdot1}$ − 0·4° [from (+)-octan-2-ol, $\alpha_D^{21\cdot4}$ + 7·72°]
*cyclo*Hexyl	Room temp.; 18 hr.	A	75	67 (8)	$n_D^{23\cdot5}$ 1·5465
Allyl	0°; 30 min.	A	84	102—103	Allyldimethylphenylammonium iodide, m. p. 85°
Crotyl	0°; 30 min.	A	83	55—56 (40—45)	Crotyldimethylphenylammonium iodide, m. p. 113—114°
Benzyl	Room temp., 1 hr.	B	95	M. p. 23°	Benzyldimethylphenylammonium iodide, m. p. 165·5°
1-Phenylethyl	Room temp., 1 hr.	C	74	7—80 (2)	—
2-Phenylethyl	Room temp., 1 hr.	B	70 †	(i) 105—107 (11) (ii) 107—111 (11) (iii) 111—115 (11)	(i) n_D^{18} 1·5830 (ii) n_D^{18} 1·5910 (iii) n_D^{18} 1·6010
1 : 3-Di-iodopropane	Room temp., 2 hr.	B	95	50—51° (0·5)	n_D^{21} 1·6420
Ethyl α-iodopropionate	Room temp., 12 hr.	A	92	65—66 (8)	(Found: I, 56·0. Calc. for $C_5H_9O_2I$: I, 55·7%) $n_D^{20\cdot5}$ 1·5000

* Pressure (mm.) in parentheses, if not 1 atm.

† In these cases, the iodide was contaminated with alcohol and the yield has been calculated from the refractive indices of the various fractions.

Cholesteryl Iodide.—Cholesterol (9·5 g.) was intimately mixed with triphenyl phosphite methiodide (12 g.); methyl iodide (10 ml.) was added and the mixture warmed to 50—60°, under reflux, for 1 hr. Next morning, the product was extracted with light petroleum (b. p. 40—60°; 100 ml.). The extract was evaporated and the residual syrup stirred with water (100 ml.); the water-insoluble fraction was washed with a little acetone and then dissolved in hot acetone (200 ml.). An oil which separated on cooling was removed and the solution kept at 2° for 2 days, whereupon it deposited cholesteryl iodide in needles, m. p. 99—100°; further crops were obtained by partial evaporation and cooling, the total yield being 3·6 g. (30%). Recrystallisation from ethyl acetate gave the pure iodide, m. p. 105°, $[\alpha]_D^{21\cdot2}$ −12·7° (*c* 3·86 in $CHCl_3$) (Found : C, 65·3; H, 9·1; I, 25·5. Calc. for $C_{27}H_{45}I$: C, 65·3; H, 9·1; I, 25·6%).

Preparation of Alkyl Chlorides from Triphenyl Phosphite Benzylochloride.—Triphenyl phosphite benzylochloride (cf. Michaelis and Kähne, *Ber.*, 1898, **31**, 1050). This was prepared by heating triphenyl phosphite (34 g.) and benzyl chloride (13 g.) at 170—175° for 60 hr. The syrupy

product was washed twice with light petroleum (b. p. 40—60°), then dried and weighed *in vacuo* (yield, 25 g.).

n-*Hexyl chloride.* *n*-Hexyl alcohol (5·5 g.) was mixed with the benzylochloride (25 g.); the exothermic reaction was moderated by cooling in ice. The mixture was then distilled under reduced pressure into a trap at −80°. The condensate (9 g.) was washed with N-sodium hydroxide and water, dried, and distilled, giving *n*-hexyl chloride (6 g., 95%), b. p. 132—136°, $n_D^{21\cdot5}$ 1·4230, characterised as *S*-*n*-hexyl*iso*thiuronium picrate, m. p. 155—156°.

2-*Chloro-octane.* Triphenyl phosphite benzylochloride (10 g.), mixed with (+)-octan-2-ol (2 g.; $\alpha_D^{21\cdot4}$ +7·72°), was kept at room temperature overnight. Distillation gave impure 2-chloro-octane which was washed with 2N-sodium hydroxide and water, dried, and distilled, yielding (−)-2-chloro-octane (1·8 g., 79%), b. p. 60°/13 mm., n_D^{20} 1·4275, $\alpha_D^{22\cdot4}$ −24·72°.

Tribenzyl Phosphite.—Phosphorus trichloride (23 g.) was added during 20 min. to a well-stirred, water-cooled mixture of benzyl alcohol (54 g.), dimethylaniline (61 g.), and anhydrous ether (100 ml.). The precipitated dimethylaniline hydrochloride was filtered off and washed thoroughly with anhydrous ether. Two fractional distillations of the filtrate and washings gave (i) dibenzyl hydrogen phosphite (8 g.), b. p. 145—160°/0·05 mm. (Found: C, 64·0; H, 5·75. Calc. for $C_{14}H_{15}O_3P$: C, 64·1; H, 5·75%), (ii) a mixture (10 g.), b. p. 160—180°/0·05 mm. (Found: C, 66·5; H, 5·9%), and (iii) *tribenzyl phosphite* (18 g., 31%), b. p. 180—195°/0·05 mm. (Found: C, 70·9; H, 6·1. $C_{21}H_{21}O_3P$ requires C, 71·6; H, 6·0%), which solidified and crystallised from light petroleum in long needles, m. p. 52° (Found: C, 71·2; H, 6·3%). No addition compound was found when tribenzyl phosphite was heated with methyl iodide at 100° for 30 hr.; the same reactants gave benzyl iodide when heated at 150° for 3 hr.

Preparation of Alkyl Halides from Triphenyl Phosphite, an Alkyl Halide, and an Alcohol.—A mixture of these reactants was refluxed, preferably by use of an electric heating-mantle, for the appropriate time. The product was worked up by one of three general methods outlined on p. 2229.

Some preparative experiments, on the 0·05—0·1-molar scale, are summarised in the annexed Tables.

Preparation of alkyl iodides.

Iodide	Iodide used (molar ratio, phosphite : iodide : alcohol), reaction conditions	Isolation	Yield (%)	B. p.*	Characterisation
Ethyl	MeI (1 : 2 : 1), steam-bath, 60 hr.	A	80	65—72°	Ethyldimethylphenylammonium iodide, m. p. 131°
n-Butyl	MeI (1·1 : 1·7 : 1), mantle, 60 hr.	A	90	129—130	n_D^{19} 1·5000
sec.-Butyl	MeI (1·1 : 1·5 : 1), mantle, 39 hr.	A	66	117—120	$n_D^{19\cdot5}$ 1·4985
1-Methylheptyl	(*a*) MeI (1 : 2·2 : 1), mantle, 24 hr.	B	76	40 (0·5)	$\alpha_D^{23\cdot6}$ −0·1° [from (+)-octan-2-ol, $\alpha_D^{21\cdot4}$ +7·72°]
,,	(*b*) MeI (1 : 6 : 1), mantle, 24 hr.	B	—	43—49 (0·7)	$\alpha_D^{15\cdot5}$ +23·5° [from (−)-octan-2-ol, $\alpha_D^{20\cdot4}$ −7·83°]
Allyl	MeI (1 : 1·5 : 1), mantle, 40 hr.	A	70	101—103	n_D^{21} 1·5540 (yield corr. for contamination with MeI); allylquinolinium iodide, m. p. 175°
2-Phenylethyl	MeI (1·1 : 1·5 : 1), mantle, 48 hr.	C	99	94—95 (1·5)	$n_D^{23\cdot5}$ 1·5990
*cyclo*Hexyl	MeI (1·1 : 1·5 : 1), mantle, 48 hr., 75—110°	B	42	63—65 (6)	n_D^{17} 1·5490
1 : 3-Di-iodo-propane	MeI (2·2 : 3 : 1), steam-bath, 30 hr.	B	80	65 (0·8)	n_D^{22} 1·6370 (redistillation gave a 46% yield of material with n_D^{20} 1·6430)
1:3-Di-iodo-2:2-dimethyl-propane	MeI (2·2 : 3 : 1), mantle, 39 hr., 75—130°	C	85	70—75 (0·9)	n_D^{17} 1·5935; I, 76·8% †
*neo*Pentyl	MeI (1 : 1·4 : 1), mantle, 24 hr., 75—130°	B	74	61—62 (50)	n_D^{23} 1·4888; ββ-dimethylbutyranilide, m. p. 129—130°
Ethyl α-iodo-propionate	MeI (1·1 : 1·5 : 1), mantle, 48 hr.	B	77	64—65 (8)	n_D^{20} 1·5000

* Pressure (mm.) in parentheses, if not 1 atm.

† Redistillation gave pure 1 : 1-*di-iodo*-2 : 2-*dimethylpropane*, b. p. 70°/1 mm., n_D^{17} 1·5950 (Found: I, 77·9. $C_5H_{10}I_2$ requires I, 78·4%).

Preparation of alkyl bromides.

Bromide	Bromide used (molar ratio, phosphite : bromide : alcohol), reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	CH_2PhBr (1·1 : 1·1 : 1), mantle, 46 hr., 140°	A	95	101°	n_D^{20} 1·4400
Allyl	CH_2PhBr (1·1 : 1·1 : 1), mantle, 48 hr., 140—130°	A	66	70—71	n_D^{21} 1·4670
1 : 3-Di-iodopropane	CH_2PhBr (2·2 : 2·2 : 1), mantle, 48 hr., 140°	B	85	70—75°/20 mm.	n_D^{17} 1·5220 *
Ethyl α-iodopropionate	CH_2PhBr (1·1 : 1·1 : 1), mantle, 62 hr., 160°	B	80	158—159	n_D^{18} 1·4445 (Found : Br, 44·2. Calc. for $C_5H_9O_2Br$: Br, 44·2%)
n-Butyl	$CH_2Br{\cdot}CO_2Et$ (1 : 1 : 1), mantle, 64 hr., 140—150°	A	58	100—102	n_D^{23} 1·4330
n-Butyl	$CH_2Br{\cdot}CH_2Br$ (1·05 : 1 : 1·05), sand-bath, 60 hr., 150°	B	40	100—122	Product contaminated with ethylene dibromide; yield calc. from n_D of the various fractions

* Redistillation gave a product, b. p. 164—165°, n_D^{18} 1·5235 (Found : Br, 79·4. Calc. for $C_3H_6Br_2$: Br, 79·25%).

Preparation of alkyl chlorides.

Chloride	Chloride used (molar ratio, phosphite : chloride : alcohol), reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	CH_2PhCl (1 : 1 : 1), mantle, 64 hr., 140—150°	A	65	78—79°	n_D^{25} 1·4010
Allyl	CH_2PhCl (1·1 : 1·1 : 1), mantle, 48 hr., 140—125°	A	59	44—45	n_D^{20} 1·4150
1 : 3-Di-iodopropane	CH_2PhCl (2·2 : 2·2 : 1), mantle, 48 hr., 170—180°	B	79	119—121	n_D^{20} 1·4470 *
Ethyl α-iodopropionate	CH_2PhCl (1·1 : 1·05 : 1), mantle, 60 hr., 175—180°	B	77	50—52°/8 mm.; 140—143	n_D^{20} 1·4220
n-Hexyl	CCl_4 (1 : 1 : 1), sand-bath, 60 hr., 150°	A	31	80—130	Contaminated with CCl_4; yield calc. from n_D of the various fractions

* Found : Cl, 63·7. Calc. for $C_3H_6Cl_2$: Cl, 62·8%. Distillation of the high-boiling residue gave diphenyl benzylphosphonate (77%), b. p. 210°/1 mm., needles, m. p. 61—62° (from light petroleum) (Found : C, 70·0; H, 5·4. Calc. for $C_{19}H_{17}O_3P$: C, 70·4; H, 5·3%)

Methyl iodide from triphenyl phosphite, n-butyl iodide, and methanol. Triphenyl phosphite (68 g., 0·22 mole), *n*-butyl iodide (40 g., 0·22 mole), and anhydrous methanol (6·4 g., 0·20 mole) were heated with an electric heating-mantle, the methyl iodide produced being continuously removed through a 3-ft. column packed with Fenske helices; the temperature of the mixture rose from 165° to 185° during the experiment (24 hr.), but the distillation temperature never exceeded 41°. The distillate (20 g.; n_D^{21} 1·5195) was washed twice with water, dried, and distilled, yielding methyl iodide (16 g., 56%), b. p. 42—43°, n_D^{20} 1·5290, characterised as trimethylphenylammonium iodide, sublimes at 215—220°.

n-Butyl bromide from triphenyl phosphite, methyl bromide, and n-butyl alcohol. Methyl bromide was passed slowly through a sintered-glass plate, into a mixture of triphenyl phosphite

(50 g., 0·16 mole) and *n*-butyl alcohol (11 g., 0·15 mole) heated under reflux with an electric heating-mantle; the temperature of the refluxing mixture fell from 155° to 135° during the experiment (12 hr.). Distillation into a trap cooled to −80°, followed by washing and redistillation through a 3-in. Fenske column, gave *n*-butyl bromide (13 g., 63%), b. p. 101·5°, n_D^{20} 1·4400.

n-*Butyl iodide from triethyl phosphite, methyl iodide, and* n-*butyl alcohol.* Triethyl phosphite (16·6 g., 0·1 mole), methyl iodide (14·2 g., 0·1 mole), and *n*-butyl alcohol (22·2 g., 0·1 mole) were heated under reflux on the steam-bath for 1 hr. Distillation gave 10 g. (64%) of somewhat impure ethyl iodide, b. p. 55—75°, n_D^{20} 1·5080, and 8·3 g. (45%) of crude *n*-butyl iodide; the latter, on redistillation gave 6·7 g. (36%) of the substantially pure iodide, b. p. 110—130°, n_D^{20} 1·4935.

Preparation of Alkyl Chlorides from Triphenyl Phosphite, Hydrogen Chloride, and an Alcohol.—A stream of dry hydrogen chloride was passed into an equimolecular mixture of triphenyl phosphite and an alcohol, usually without cooling, until there appeared to be no further reaction. The reaction product was then worked up by one of the standard procedures (p. 2229).

Some preparative experiments on the 0·1-molar scale are summarised in the following Table.

Chloride	Reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	No cooling, 1·5 hr.	A	76	77—79°	n_D^{17} 1·4025
Allyl	No cooling, 1·5 hr.	A	46	45—46	n_D^{20} 1·4160
Crotyl	No cooling, 1·5 hr.	A	72	80—85	$n_D^{21\cdot5}$ 1·4325 (mainly crotyl chloride, but contained some 1-methylallyl chloride)
1-Methylheptyl	Phosphite–alcohol mixture kept overnight before passage of HCl for 1 hr.	B	44	53—56°/ 8—10 mm	$\alpha_D^{22\cdot2}$ + 18·8° [from (−)-octan-2-ol, $\alpha_D^{20\cdot4}$ − 7·83°]
2-Phenylethyl	No cooling, 2 hr.	C	76	82—84°/ 10—12 mm.	—

Cholesteryl chloride. Dry hydrogen chloride was passed for 30 min. through a mixture of triphenyl phosphite (5 g.) and cholesterol (2 g.), stirred at 60—70°; a clear yellow solution was obtained after a few min. The product was treated with acetone (20 ml.), and the cholesteryl chloride (1 g.) which separated filtered off and washed with acetone; dilution of this filtrate with water gave a further 1·2 g. of chloride. Recrystallisation from ethyl acetate gave pure cholesteryl chloride in needles, m. p. 95°, $[\alpha]_D^{20}$ −33·3° (*c* 3·188 in $CHCl_3$) (Found: C, 79·95; H, 11·1; Cl, 8·65. Calc. for $C_{27}H_{45}Cl$: C, 79·95; H, 11·1; Cl, 8·75%); there was no depression of m. p. on admixture with authentic (chromatographically purified) cholesteryl chloride having m. p. 94° and $[\alpha]_D^{20}$ −32·6° (*c* 3·224 in $CHCl_3$).

Preparation of Alkyl Halides from Triphenyl Phosphite, an Alcohol, and Inorganic Halides.—n-*Butyl chloride from ammonium chloride.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and ammonium chloride (6 g.) were heated under reflux at 140° for 84 hr.; ammonia was evolved during the reaction. The filtered product was distilled, giving 5·8 g. (63%) of *n*-butyl chloride, b. p. 77—78°, n_D^{22} 1·4015.

n-*Butyl chloride from sodium chloride.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and sodium chloride (6 g.) were heated at 170—180° for 120 hr. Distillation gave 1·5 g. (16%) of *n*-butyl chloride, b. p. 78°, n_D^{23} 1·4015.

n-*Butyl bromide from lithium bromide.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and lithium bromide (9·6 g.) were heated at 140° for 64 hr. Distillation gave 5·5 g. (40%) of *n*-butyl bromide, b. p. 101—102°, n_D^{24} 1·4395.

n-*Butyl iodide from sodium iodide.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and sodium iodide (16·5 g.) were heated at 160—170° for 64 hr. Distillation yielded 3·4 g. (18·5%) of *n*-butyl iodide, b. p. 130—132°, n_D^{25} 1·4980.

Reaction between Triphenyl Phosphite Methiodide and Ethanol in the Presence of Dimethylaniline.—A mixture of triphenyl phosphite methiodide (7·0 g.), absolute ethanol (1·5 g.), and dimethylaniline (3 g.) was warmed on the steam-bath for 15 min. Dilution with ether yielded ethyldimethylphenylammonium iodide (3·8 g., 88%), m. p. 115—117°, raised to 131° (not depressed on admixture with an authentic specimen) on recrystallisation from ethanol.

Ester Interchange between Triphenyl Phosphite and n-*Butyl Alcohol.*—(*a*) Triphenyl phosphite (68 g., 0·22 mole) and *n*-butyl alcohol (14·8 g., 0·20 mole) were heated at 100° for 16 hr. Fractionation gave (i) 18·5 g., b. p. 60—80°/10 mm., mainly phenol (0·20 mole), (ii) 7·5 g., b. p. 80—120°/10 mm., n_D^{25} 1·4580, mainly tri-*n*-butyl phosphite (0·03 mole) (Found: C, 57·2; H,

9·4. Calc. for $C_{12}H_{27}O_3P$: C, 57·6; H, 10·1%), (iii) 7·8 g., b. p. 120—140°/10 mm., n_D^{25} 1·4840, a mixture of tri-*n*-butyl and di-*n*-butyl phenyl phosphites (Found: C, 59·8; H, 8·4. Calc. for $C_{14}H_{23}O_3P$: C, 62·2; H, 8·6%), (iv) 9·0 g., b. p. 140—170°/10 mm., n_D^{25} 1·5302, mainly *n*-butyl diphenyl phosphite (0·03 mole) (Found: C, 64·8; H, 6·9. Calc. for $C_{16}H_{19}O_3P$: C, 66·2; H, 6·6%), (v) 4·1 g., b. p. 170—180°/10 mm., n_D^{25} 1·5819, a mixture of *n*-butyl diphenyl and triphenyl phosphites, and (vi) 28 g., residue, n_D^{25} 1·5815, similar to (v) (authentic triphenyl phosphite had n_D^{25} 1·5975).

(*b*) Triphenyl phosphite (68 g., 0·22 mole) was mixed with *n*-butyl alcohol (14·8 g., 0·20 mole) and the mixture kept at room temp. for 30 min. Distillation gave 18 g. (96%) of phenol, b. p. 60—110°/10 mm., and a mixture of phosphites which was heated under reflux for 3 hr. with methyl iodide (13 g.); distillation into a trap cooled at −80° gave *n*-butyl iodide (13 g., 35%), n_D^{23} 1·4990. The residue was heated with more methyl iodide (28 g.) for 24 hr. Distillation then gave a further 15·1 g. (41%) of *n*-butyl iodide, b. p. 125—131°, n_D^{23} 1·4980.

Reaction between Triphenyl Phosphite Methiodide and Dimethyl Methylphosphonate.—A mixture of triphenyl phosphite methiodide (23 g.) and dimethyl methylphosphonate (3 g.) was heated under reflux for 1 hr., the internal temperature falling from 120° to 100°. Distillation gave 5 g. of rather impure methyl iodide, b. p. 42—44°, n_D^{20} 1·5055, characterised as trimethylphenylammonium iodide, platelets (from alcohol), subliming at 220°.

*Reaction between Triphenyl Phosphite Methiodide and Tri-*n*-butyl Phosphite.*—Tri-*n*-butyl phosphite (2·5 g.) was added to triphenyl phosphite methiodide (5 g.); the methiodide dissolved readily on shaking, with some evolution of heat. Distillation gave *n*-butyl iodide (1·8 g., 88%), b. p. 125—132°, n_D^{23} 1·4970.

Preparation and Reactions of Some Mixed Trialkyl Phosphites.—Ethyl dimethyl phosphite. A mixture of ethyl phosphorodichloridite (147 g.; b. p. 117—118°) (Razumov, *J. Gen. Chem., U.S.S.R.*, 1944, **14**, 464) and anhydrous ether (500 ml.) was cooled in a freezing-mixture and treated portionwise, under a condenser, with a suspension of sodium methoxide (from powdered sodium, 46 g., and anhydrous methanol, 64 g.) in anhydrous ether (500 ml.). After the addition was complete, the mixture was kept at room temperature, with occasional shaking, for 1 hr.; sodium chloride was then filtered off rapidly and washed with anhydrous ether. Distillation of the filtrate and washings yielded the crude ester (107 g., 77%), b. p. 60—70°/10 mm., which, on refractionation through a 3-ft., vacuum-jacketed, Fenske column, gave pure *ethyl dimethyl phosphite* (56 g., 40·5%), b. p. 124—127° (Found: C, 34·7; H, 8·1%; equiv., 138·0. $C_4H_{11}O_3P$ requires C, 34·7; H, 8·0%; equiv., 138·0). [This equivalent, like the others quoted below, was determined as follows:—The ester (*ca.* 150 mg.) was heated at 100° under reflux with 70% alcoholic N-sodium hydroxide (5 ml.) for 1 hr.; the excess of alkali was back-titrated, after dilution, with 0·1N-hydrochloric acid (bromophenol-blue); with this indicator only one acidic group of phosphorous acid is titrated. In our experience equivalents are better criteria of purity of alkyl phosphites than elementary analyses, which often give unsatisfactory and non-concordant results.]

Ethyl dimethyl phosphite (27·6 g.) was heated under reflux for 1 hr. with methyl iodide (28·4 g.). Fractional distillation gave methyl iodide (27·5 g., 97%), b. p. 42·5—43°, characterised as trimethylphenylammonium iodide, m. p. 218—220°, and methylpyridinium iodide, m. p. 116—117°, and *ethyl methyl methylphosphonate* (27·0 g., 98%), b. p. 74—75°/15 mm. (Found: C, 34·3; H, 8·0%; equiv., 137·8. $C_4H_{11}O_3P$ requires C, 34·7; H, 8·0%; equiv., 138·0).

Ethyl dimethyl phosphite (13·8 g.) was stirred with water (2·0 g.) in acetone (10 ml.) for 30 min.; hydrolysis was accompanied by the evolution of heat. After 1 hr., distillation gave three phosphorus-containing fractions: (i) b. p. 65—73°/15—17 mm., 1·3 g. (Found: equiv., 123·5), (ii) b. p. 73—75°/15—17 mm., 9·0 g. (Found: C, 28·9; H, 7·0%; equiv., 124·0), and (iii) b. p. 75—77°/15—17 mm., 1·3 g. (Found: equiv., 126·4). Fraction (ii) was clearly *ethyl methyl hydrogen phosphite* ($C_3H_9O_3P$ requires C, 29·05; H, 7·25%; equiv., 124·0), and fractions (i) and (iii) were less pure samples of it; the total yield was 93·5%.

Diethyl methyl phosphite. The preparation of this mixed ester from diethyl phosphorochloridite and sodium methoxide or from ethyl phosphorodichloridite or phosphorodibromidite and sodium ethoxide was unsatisfactory. The following was the procedure finally adopted:

A mixture of anhydrous methanol (32 g.) and dimethylaniline (121 g.) was added, with ice-cooling, during 1 hr., to a well-stirred mixture of phosphorus trichloride (137 g.) and anhydrous ether (1 l.). Next, a mixture of anhydrous ethanol (92 g.) and dimethylaniline (242 g.) was added similarly during 2 hr. More ether (500 ml.) was then added and the dimethylaniline hydrochloride filtered off and washed twice with anhydrous ether. The filtrate and washings were distilled and the fraction of b. p. 50—90°/10—15 mm. was twice refractionated through a

3-ft. Fenske column, yielding *diethyl methyl phosphite* (35 g., 23%), b. p. 136—139° (Found: C, 38·6; H, 8·5%; equiv., 152·6. $C_5H_{13}O_3P$ requires C, 39·5; H, 8·55%; equiv., 152·0).

Diethyl methyl phosphite (10 g.) and methyl iodide (8·5 g.) were refluxed on the steam-bath for 30 min. Distillation gave methyl iodide (6·8 g., 79%), b. p. 41—50°, characterised as trimethylphenylammonium iodide, m. p. 215°, and methylpyridinium iodide, m. p. 116°, and diethyl methylphosphonate (6 g., 60%), b. p. 190—192°, n_D^{23} 1·4110 (Found: C, 38·1; H, 8·6%; equiv., 152·0. Calc. for $C_5H_{13}O_3P$: C, 39·5; H, 8·55%; equiv., 152·0).

Diethyl methyl phosphite (10 g.) was heated on the steam-bath for 30 min. with water (1·5 g.) in acetone (10 ml.). Distillation gave 5·3 g. (58%) of diethyl hydrogen phosphite, b. p. 65—66°/8 mm., n_D^{21} 1·4070 (Found: C, 33·2; H, 7·7%; equiv., 137·2. Calc. for $C_4H_{11}O_3P$: C, 34·75; H, 8·0%; equiv., 138·0).

Ethyl diisopropyl phosphite. A mixture of *iso*propyl alcohol (120 g.) and dimethylaniline (242 g.) was added during 80 min. to a well-stirred, ice-cooled mixture of ethyl phosphorodichloridite (130 g.) and anhydrous ether (500 ml.). After the mixture had been stirred at room temperature for a further 30 min., the dimethylaniline hydrochloride was filtered off and washed with ether. Removal of the ether and fractionation of the residue through a 3-ft. Fenske column gave *ethyl diisopropyl phosphite* (97 g., 50%), b. p. 69—71°/10 mm. (Found: C, 49·7; H, 10·05%; equiv., 192·1. $C_8H_{19}O_3P$ requires C, 49·5; H, 9·9%; equiv., 194·0).

This ester (19·5 g.) was refluxed at 100° for 30 min. with methyl iodide (14·2 g.); the reaction was very vigorous. Distillation gave ethyl iodide (12 g., 77%), b. p. 71—73°, n_D^{20} 1·5125, and di*iso*propyl methylphosphonate (17 g., 94%), b. p. 75—76°/5 mm., n_D^{20} 1·4158 (Found: C, 46·8; H, 9·35. Calc. for $C_7H_{17}O_3P$: C, 46·7; H, 9·5%).

Ethyl di*iso*propyl phosphite (19·5 g.) and water (2 g.) in acetone (10 ml.) were refluxed on the steam-bath for 14 hr. Distillation gave di*iso*propyl hydrogen phosphite (12·5 g., 75%), b. p. 89—90°/10 mm. (Found: C, 42·9; H, 9·3%; equiv., 159·3. Calc. for $C_6H_{13}O_3P$: C, 43·4; H, 9·1%; equiv., 166·0).

The majority of the microanalyses were carried out under the direction of Mr. F. H. Oliver in the microanalytical laboratory of the Organic Chemistry Department, Imperial College.

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459. *Hydropteridines. Part I. The Formation of 5 : 6 : 7 : 8-Tetrahydro-4 : 6-dimethylpteridines.*

By J. H. Lister and G. R. Ramage.

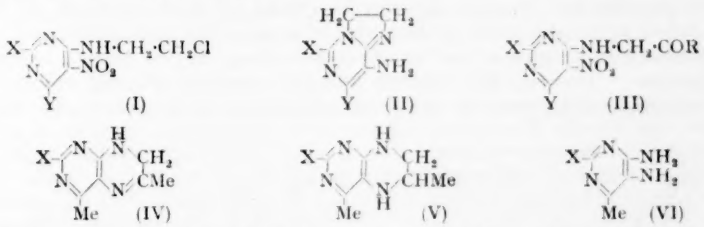
Reduction and cyclisation of 4-acetonylamino-6-methyl-5-nitropyrimidines give 7 : 8-dihydro-4 : 6-dimethylpteridines which can be further reduced to 5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridines. These have been characterised by comparing their ultra-violet spectra with those of the corresponding 4 : 5-diamino-6-methylpyrimidines.

Recent developments in the chemotherapy of anæmia have shown that the liver factor isolated by Sauberlich and Baumann (*J. Biol. Chem.*, 1948, **176**, 165), capable of supporting *Leuconostoc citrovorum* 8081, contains a reduced pteridine nucleus. This factor may undergo oxidative changes during extraction to give pteroylglutamic acid (May, Bardos, Barger, Lansford, Ravel, Sutherland, and Shive, *J. Amer. Chem. Soc.*, 1951, **73**, 3067). Simpler reduced pteridines, *e.g.* dihydro- and tetrahydro-pteridines, and the conditions necessary for their oxidation to pteridines are being investigated.

Of various possible routes to tetrahydropteridines (V) under examination one has been reported. The cyclisation of some 4-2′-chloroethylaminopyrimidines (I) gave, however, glyoxalinopyrimidines (II), and not derivatives of pteridine (Ramage and Trappe, *J.*, 1952, 4410).

Some 5-nitro-4-pyrimidylaminoacetic esters (III; R = OEt) (Boon, Jones, and Ramage, *J.*, 1951, 96) and the corresponding acetone compounds (III; R = Me) Boon and Jones,

ibid., p. 591) gave dihydropteridines on reduction. Other hydro-derivatives have been prepared from 6 : 7-dimethyl- and 6 : 7-diphenyl-pteridine by reduction (Polonovski, Pesson, and Puister, *Compt. rend.*, 1950, **230**, 2205).



The present experiments are based on the condensation of 2 : 4-dichloro-6-methyl-5-nitropyrimidine with aminoacetone, giving 4-acetonylamino-2-chloro-6-methyl-5-nitropyrimidine (III; R = Me, X = Cl, Y = Me). This was catalytically reduced in ethanol in the presence of Raney nickel, best at 55°. After removal of the catalyst from the hot solution and cooling, 2-chloro-7 : 8-dihydro-4 : 6-dimethylpteridine (IV; R = Me, X = Cl) crystallised. Boon and Jones (*loc. cit.*) reported that they were unable to isolate this product.

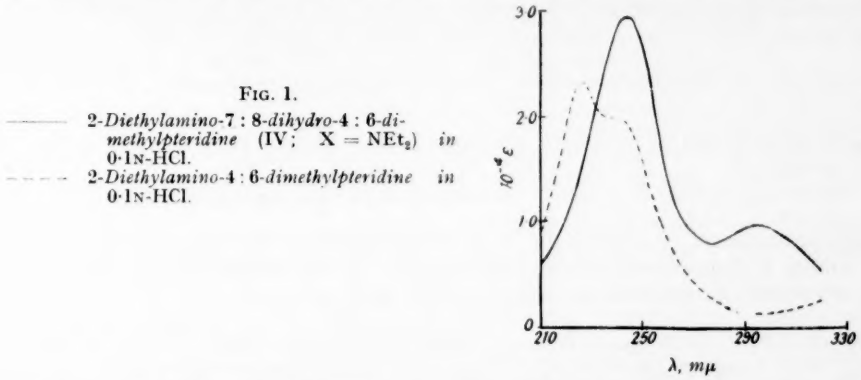


FIG. 1.

——— 2-*Diethylamino*-7 : 8-*dihydro*-4 : 6-*dimethylpteridine* (IV; X = NEt_2) *in* 0·1N-HCl.

– – – – 2-*Diethylamino*-4 : 6-*dimethylpteridine in* 0·1N-HCl.

Other 2-substituted 7 : 8-dihydro-4 : 6-dimethylpteridines have been prepared similarly, the required substituents being introduced before the reduction and cyclisation. Dilute acid hydrolysis of 4-acetonylamino-2-chloro-6-methyl-5-nitropyrimidine gave the 2-hydroxypyrimidine (III; R = Me, X = OH, Y = Me) whereas alcoholic ammonia, or primary or secondary amine gave (III; R = Me, X = NH_2 or substituted amino, Y = Me), and with alcoholic sodium hydrogen sulphide (III; R = Me, X = SH, Y = Me) was obtained. These were reduced in alcohol with hydrogen in the presence of Raney nickel whereupon cyclisation to the dihydropteridine occurred.

The reduction of the dihydropteridines, in glacial acetic acid, in the presence of platinum oxide has been used generally for the preparation of 2-substituted 5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridines. Even the 2-chloro-derivative (IV; X = Cl) took up one mole of hydrogen to give 2-chloro-5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridine (V; X = Cl), and no ionic chlorine could be detected. However, further reduction in ethanol, in the presence of palladium–charcoal, gave a hydrochloride from which 5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridine (V; X = H) was obtained by treatment with concentrated alkali.

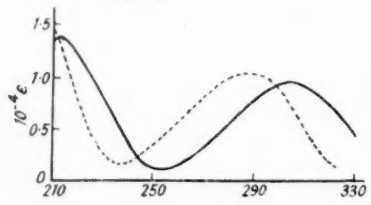
It was preferable to reduce some dihydropteridines in alcohol, under pressure, in the presence of Raney nickel, to the tetrahydropteridine, *e.g.* 2-diethylamino-7 : 8-dihydro-4 : 6-dimethylpteridine (IV; X = NEt_2) was smoothly reduced at 60 atm. to 2-diethylamino-5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridine (V; X = NEt_2).

The 7 : 8-dihydro-4 : 6-dimethylpteridines were unstable in both 0·1N-acid and 0·05N-

alkali, oxidation back to the pteridine rapidly occurring on short exposure to the atmosphere. This conversion was followed by periodic examination of the ultra-violet spectra and comparisons of the final curves with those of the pteridines themselves (Fig. 1). In contrast no change occurred during the ageing of acid solutions of the tetrahydropteridines, and reproducible spectra were obtained after some weeks.

From the structural aspect, the tetrahydropteridines can be related to the 4 : 5-diaminopyrimidines. The two give almost identical spectra, differing only in that the bands of maximum absorption in the tetrahydropteridines are moved to longer wave-

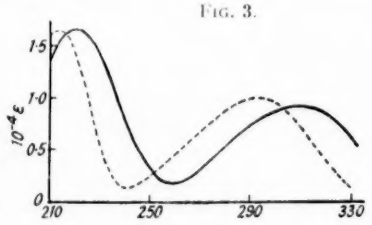
FIG. 2.



——— 5 : 6 : 7 : 8-*Tetrahydro*-4 : 6-*dimethylpteridine* (V; X = H) *in* 0·1N-HCl.

– – – – 4 : 5-*Diamino*-6-*methylpyrimidine* (VI; X = H) *in* 0·1N-HCl.

FIG. 3.



——— 2-*Chloro*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine* (V; X = Cl) *in* 0·1N-HCl.

····· 4 : 5-*Diamino*-2-*chloro*-6-*methylpyrimidine* (VI; X = Cl) *in* 0·1N-HCl.

lengths (Figs. 2 and 3), and such comparisons have proved to be a useful method of characterisation.

The hydropteridines described did not appear to form characteristic derivatives.

Comparative spectra of 2-*substituted* 5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridines* (V) *and related* 4 : 5-*diamino*-6-*methylpyrimidines* (VI), *in* 0·1N-*hydrochloric acid* (*wave-lengths are in* mμ; *the values in parentheses are* $10^{-4}\ \varepsilon_{max.}$).

X	(V) Max.		Min.	(VI) Max.		Min.
OH	230 (0·993)	325 (0·698)	270 (0·203)	214 (1·25)	293 (0·787)	255 (0·207)
H	213 (1·36)	306 (0·936)	254 (0·112)	<210	288 (1·04)	238 (0·188)
Cl	221 (1·66)	310 (0·910)	258 (0·170)	214 (1·63)	292 (0·983)	241 (0·146)
NEt_2	235 (2·58)	—	—	233 (2·87)	290 (0·277)	274 (0·234)
NH_2	212 (2·08)	233 (1·12)	228 (1·11)	<210	277 (0·478)	261 (0·412)

7 : 8-*Dihydro*-4 : 6-*dimethylpteridines* (IV), *in* 0·1N-*hydrochloric acid.*

X	Max.		Min.
OH	<210 (—)	284 (1·24)	241 (0·278)
Cl	217 (2·48)	302 (0·7) (approx.)	256 (0·199)
NEt_2	244 (2·90)	295 (0·956)	276 (0·782)
NH_2	226 (3·17)	291 (1·02)	260 (0·444)

The determinations were made by means of a Unicam S.P. 500 quartz spectrophotometer (kindly lent by the Wool Textile Research Council).

EXPERIMENTAL

4-*Acetonylamino*-2-*amino*-6-*methyl*-5-*nitropyrimidine*.—4-Acetonylamino-2-chloro-6-methyl-5-nitropyrimidine (2 g.) (Boon and Jones, *loc. cit.*) was dissolved in warm ethanol and treated with ammonia solution (*d* 0·88; 6 c.c.). The solution was boiled under reflux for 25 min. and, on cooling in ice-water, 4-*acetonylamino*-2-*amino*-6-*methyl*-5-*nitropyrimidine* (1·1 g., 60%) separated as brown prisms, m. p. 198—200° (decomp.), from water (Found: C, 42·2; H, 5·1. $C_8H_{11}O_3N_5$ requires C, 42·7; H, 4·9%).

4-*Acetonylamino*-2-*diethylamino*-6-*methyl*-5-*nitropyrimidine*.—4-Acetonylamino-2-chloro-6-

methyl-5-nitropyrimidine (5 g.) in ethanol (80 c.c.) was treated with diethylamine (5 c.c.) dropwise, with shaking. The lemon-yellow needles (5·2 g., 90%) which quickly separated had m. p. 117—118°.

4-*Acetonylamino*-2-*hydroxy*-6-*methyl*-5-*nitropyrimidine*.—The 2-chloro-6-methyl-5-nitropyrimidine (3·0 g.) was refluxed in glacial acetic acid (20 c.c.) for 20 min. On cooling of the solution 4-*acetonylamino*-2-*hydroxy*-6-*methyl*-5-*nitropyrimidine* (2·4 g., 87%) separated and was filtered off and washed with dilute acetic acid; it formed needles (from water), m. p. 245° (decomp.) (Found: C, 42·9; H, 4·0. $C_8H_{10}O_4N_4$ requires C, 42·5; H, 4·45%).

2-*Chloro*-7 : 8-*dihydro*-4 : 6-*dimethylpteridine*.—4-Acetonylamino-2-chloro-6-methyl-5-nitropyrimidine (5 g.), in warm ethanol (100 c.c.), was hydrogenated at 45—50° and atmospheric pressure in the presence of Raney nickel catalyst (8 c.c.; settled suspension); hydrogen uptake was complete after 50 min. Cooling the concentrated filtrate gave 2-*chloro*-7 : 8-*dihydro*-4 : 6-*dimethylpteridine* (3·1 g., 77%) as plates, m. p. 215° (decomp.), from ethanol (Found: C, 48·6; H, 4·3. $C_8H_9N_4Cl$ requires C, 48·9; H, 4·6%).

2-*Amino*-7 : 8-*dihydro*-4 : 6-*dimethylpteridine*.—A suspension of 4-acetonylamino-2-amino-6-methyl-5-nitropyrimidine (2·53 g.) in ethanol (175 c.c.) was shaken with Raney nickel (10 c.c., settled suspension) in hydrogen; theoretical uptake was reached in about 90 min. The combined filtrate and washings were concentrated under reduced pressure; the resulting 2-amino-7 : 8-dihydro-4 : 6-dimethylpteridine (1·75 g.) formed brown prisms, m. p. 200° (decomp.), from water (Found: C, 49·2; H, 6·9. $C_8H_{11}N_5,H_2O$ requires C, 49·2; H, 6·7%).

2-*Diethylamino*-7 : 8-*dihydro*-4 : 6-*dimethylpteridine*.—4-Acetonylamino-2-diethylamino-6-methyl-5-nitropyrimidine (3 g.) was reduced as described for the 2-amino-compound, giving orange-yellow needles (2·0 g., 80%), m. p. 124—125°, from ligroin. Boon and Jones (*loc. cit.*) report m. p. 121°.

7 : 8-*Dihydro*-2-*hydroxy*-4 : 6-*dimethylpteridine*.—4-Acetonylamino-2-hydroxy-6-methyl-5-nitropyrimidine (1·9 g.), suspended in aqueous ethanol (75 c.c.), was hydrogenated over Raney nickel (4 c.c., settled suspension) at 50° for 30 min. The combined filtrate and aqueous washings on cooling deposited 7 : 8-*dihydro*-2-*hydroxy*-4 : 6-*dimethylpteridine* as needles (from water), which turned black but did not melt at 250° and decomposed at 294° (Found: C, 54·1; H, 5·7. $C_8H_{10}ON_4$ requires C, 53·9; H, 5·7%).

2-*Chloro*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine*.—2-Chloro-7 : 8-dihydro-4 : 6-dimethylpteridine (2 g.), in acetic acid (50 c.c.), was hydrogenated at atmospheric temperature and pressure over Adams's catalyst (0·1 g.). Uptake ceased at 1 mol. of hydrogen after 5 hr. Evaporation of the filtered solution under reduced pressure in an atmosphere of hydrogen gave a residue which was washed with a little methanol and crystallised from amyl alcohol, giving 2-*chloro*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine* (1·55 g., 77%) as salmon-pink needles, m. p. 226—227° (Found: C, 48·6; H, 5·9; Cl, 17·9. $C_8H_{11}N_4Cl$ requires C, 48·4; H, 5·6; Cl, 17·9%). It gave no precipitate with mercuric chloride solution.

5 : 6 : 7 : 8-*Tetrahydro*-4 : 6-*dimethylpteridine*.—Hydrogenation of 2-chloro-5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridine (1·5 g.) in ethanol (100 c.c.) in the presence of palladium–charcoal (2·0 g., 10%) proceeded smoothly with the absorption of 1 mol. of hydrogen. The combined filtrate and washings (hot ethanol) gave on evaporation a pinkish-white, crystalline hydrochloride (1·4 g.), m. p. 231° (from amyl alcohol).

The *base* (0·7 g., 56%), on crystallisation from ligroin containing a little ethyl acetate, formed pink prisms, m. p. 159° (Found: C, 58·4; H, 7·4; N, 34·2. $C_8H_{12}N_4$ requires C, 58·5; H, 7·4; N, 34·1%). It gave a product, m. p. 252—253°, with picric acid, and a white precipitate with mercuric chloride solution.

2-*Amino*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine*.—2-Amino-7 : 8-dihydro-4 : 6-dimethylpteridine (0·25 g.) was hydrogenated over Adams's catalyst (0·03 g.) in glacial acetic acid, as for the 2-chloropteridine. Removal of the solvent left a red oil which crystallised in contact with 50% potassium hydroxide solution. 2-*Amino*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine* formed brown prisms (0·15 g., 60%), m. p. 206—207°, from water (Found: C, 51·3; H, 7·5; N, 36·8. $C_8H_{13}N_5,\frac{1}{2}H_2O$ requires C, 51·1; H, 7·5; N, 37·2%). It gave a yellow precipitate with mercuric chloride solution; the picrate had m. p. 270° (decomp.).

2-*Diethylamino*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine*.—2-Diethylamino-7 : 8-dihydro-4 : 6-dimethylpteridine (2 g.) in ethanol (200 c.c.) was reduced at 45 atmospheres' pressure with hydrogen and Raney nickel (7 c.c., settled suspension) for 10 hr. Removal of the catalyst gave a straw-coloured solution with a blue fluorescence, from which the alcohol was removed under reduced pressure in an atmosphere of hydrogen, leaving a brown oil which slowly crystallised. 2-*Diethylamino*-5 : 6 : 7 : 8-*tetrahydro*-4 : 6-*dimethylpteridine* formed brown prisms,

m. p. 93° (1·7 g., 84%), from ligroin containing a little ethyl acetate, or from aqueous acetone (Found: C, 61·4; H, 8·7. $C_{12}H_{21}N_5$ requires C, 61·2; H, 9·0%).

5 : 6 : 7 : 8-*Tetrahydro-2-hydroxy-4* : 6-*dimethylpteridine*.—The hydrogenation of 7 : 8-dihydro-2-hydroxy-4 : 6-dimethylpteridine (1·15 g.) in acetic acid (50 c.c.) over Adams's catalyst (0·03 g.) for 5 hr. gave 5 : 6 : 7 : 8-*tetrahydro-2-hydroxy-4* : 6-*dimethylpteridine* as needles, which blackened without melting around 300° (Found: C, 53·8; H, 6·7; N, 30·2. $C_8H_{12}ON_4$ requires C, 53·3; H, 6·7; N, 31·1%). The picrate had m. p. 235° (decomp.).

2-*Diethylamino-4* : 6-*dimethylpteridine*.—(*a*) A solution of potassium permanganate (1 g.) in dry acetone (500 c.c.) was added dropwise with stirring to 2-diethylamino-7 : 8-dihydro-4 : 6-dimethylpteridine (2 g.) in dry acetone (100 c.c.). The addition was complete after 2 hr. and stirring was continued for a further 2 hr. The solvent was evaporated from the filtered solution leaving a red oil which slowly crystallised. 2-*Diethylamino-4* : 6-*dimethylpteridine* (1·8 g., 91%) formed red prisms, m. p. 87—88°, from light petroleum (b. p. 40—60°) (Found: C, 62·4; H, 7·3. $C_{12}H_{17}N_5$ requires C, 62·3; H, 7·4%).

(*b*) 2-Diethylamino-5 : 6 : 7 : 8-tetrahydro-4 : 6-dimethylpteridine (0·5 g.) was oxidised with permanganate (0·5 g.) as above; removal of the acetone gave 2-diethylamino-4 : 6-dimethylpteridine (0·2 g.), m. p. 87—88° alone and on admixture with the sample prepared as in (*a*). The identity was confirmed by the ultra-violet spectrum.

4-*Amino-2-diethylamino-6-methyl-5-nitropyrimidine*.—4-Amino-2-chloro-6-methyl-5-nitropyrimidine (1 g.) was dissolved in ethanol (50 c.c.), and diethylamine (1·5 c.c.) added. The solution was evaporated to dryness and the yellow residue crystallised from water–ethanol (4 : 1) giving 4-*amino-2-diethylamino-6-methyl-5-nitropyrimidine* as yellow needles, m. p. 73—74° (Found: C, 48·4; H, 6·8. $C_9H_{15}O_2N_5$ requires C, 48·0; H, 6·7%).

4 : 5-*Diamino-2-diethylamino-6-methylpyrimidine*.—4-Amino-2-diethylamino-6-methyl-5-nitropyrimidine (0·2 g.) in ethanol (30 c.c.) was hydrogenated with Raney nickel (1 c.c., settled suspension), uptake being complete in 4 hr. The solution was filtered and concentrated under reduced pressure, leaving a pale brown solid. This was crystallised from ligroin giving 4 : 5-*diamino-2-diethylamino-6-methylpyrimidine* (0·1 g., 58%), m. p. 97° (Found: C, 55·3; H, 8·6. $C_9H_{17}N_5$ requires C, 55·4; H, 8·8%).

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THE TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, March 11th*, 1953.]

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460. *A Modified Benziminazole Synthesis.*

By E. S. LANE.

Reaction of aliphatic diamides with *o*-diamines or their salts is shown to produce bisbenziminazoles, including a number which cannot be obtained by the conventional route from the dicarboxylic acid. Some extensions of the reaction are reported.

LITTLE work has been reported on the preparation of benziminazoles from carboxyamides and *o*-diamines despite the good yields that have been obtained in this reaction (Wright, *Chem. Reviews*, 1951, **48**, 397, and references therein). In order to provide a simpler route to some difunctional benziminazole derivatives (required for metal-complex investigations), the reaction between some aliphatic diamides and *o*-diamines has been examined. Whereas oxalic acid or its esters with *o*-diamines give 2 : 3-dihydroxyquinoxalines (Phillips, *J.*, 1928, 2397), oxamide and *o*-phenylenediamine or 3 : 4-diaminotoluene have now been shown to give, respectively, 2 : 2′-dibenziminazolyl and 5 : 5′-dimethyl-2 : 2′-dibenziminazolyl. The former compound has previously been obtained by the reduction of *oo*′-dinitro-oxanilide (Hübner, *Annalen*, 1881, **209**, 339), and the latter by the reduction of *NN*′-di-(4-methyl-2-nitrophenyl)oxamide (Hübner, *ibid.*, p. 370) and by heating *NN*′-di-(2-amino-4-methylphenyl)oxamide (Hinsberg, *Ber.*, 1882, **15**, 2690). The powerful fluorescence of solutions of these compounds and particularly of their salts is now noted.

Conventional syntheses of bisbenziminazoles from dibasic acids or esters also fail in the

case of malonic acid or esters, which with *o*-phenylenediamine form *o*-phenylenemalonamide (Shriner and Boermans, *J. Amer. Chem. Soc.*, 1944, **66**, 1810; Phillips, *ibid.*, 1942, **64**, 187). Malonamide with *o*-phenylenediamine, however, gives methylenebis-2-benziminazole. This synthesis proceeded readily when the *o*-diamine or its salts and the diamide were heated together, preferably in a high-boiling solvent, *e.g.*, ethylene glycol or glycerol. *NN'*-Di-(2-hydroxethyl)diamides, which, in some cases, are more conveniently prepared than the unsubstituted diamides, may also be used, as may the ammonium salts of the acids. The scope of the reaction, which may be regarded as an extension of the acylation method of Galat and Elion (*J. Amer. Chem. Soc.*, 1943, **65**, 1566), is shown below.

Equimolecular quantities of *NN'*-di-(2-hydroxyethyl)oxamide and *o*-phenylenediamine under similar conditions gave, uniquely, benziminazole-2-carboxy-2'-hydroxyethylamide. The 5-methyl homologue was similarly obtained from 3 : 4-diaminotoluene. This route to these compounds is considerably simpler than that described by Copeland and Day (*J. Amer. Chem. Soc.*, 1943, **65**, 1072) for the former compound.

Experimental

NN'-Di-(2-hydroxyethyl)diamides were prepared by Rauscher and Clark's method (*J. Amer. Chem. Soc.*, 1948, **70**, 438).

2 : 2'-*Dibenziminazolyl.*—Oxamide (4·4 g.), *o*-phenylenediamine (10·8 g.), and ethylene glycol (10 ml.) were refluxed for 3 hr., then cooled and poured into water (200 ml.). The yellow insoluble material was filtered off (9·2 g.) and recrystallised (charcoal) from ethylene glycol, yielding 2 : 2'-dibenziminazolyl as a yellow microcrystalline powder which shrank with decomposition at 395—400° but did not completely melt (Found: C, 71·6; H, 4·4; N, 24·0. Calc. for $C_{14}H_{10}N_4$: C, 71·8; H, 4·3; N, 23·95%). Hübner (*loc. cit.*) reported that it did not melt at 300°.

Ammonium oxalate monohydrate (3·6 g.), *o*-phenylenediamine (5·5 g.), and glycerol (10 g.) were refluxed together for 2 hr., then poured into water (100 ml.), and the 2 : 2'-dibenziminazolyl was filtered off and recrystallised from ethylene glycol (yield 2·0 g.).

5 : 5'-*Dimethyl*-2 : 2'-*dibenziminazolyl.*—Oxamide (4·4 g.), 3 : 4-diaminotoluene (12·2 g.), and ethylene glycol (15 g.) similarly formed 5 : 5'-dimethyl-2 : 2'-dibenziminazolyl (6·4 g.), which crystallised from ethanol as fine yellow needles, m. p. 350° (with sublimation, in an open tube) (Found: N, 22·0. Calc. for $C_{16}H_{14}N_4$: N, 21·35%). Hübner (*loc. cit.*) gives m. p. "about 193°."

Ammonium oxalate monohydrate (1·7 g.), 3 : 4-diaminotoluene (3·7 g.), and glycerol (5 g.) similarly yielded this compound (2·4 g.), m. p. 345—350°.

Methylenebis-2-*benziminazole.*—Malonamide (5·1 g.), *o*-phenylenediamine (10·8 g.), and ethylene glycol (15 ml.) were refluxed together for 4 hr., then poured into water, and the solid formed (5·2 g.) was filtered off. Recrystallisation (charcoal) from ethylene glycol gave colourless prisms of *methylenebis*-2-*benziminazole*, m. p. 389° (decomp.; bath preheated to 370°) (Found: C, 72·5; H, 5·3; N, 22·2. $C_{15}H_{12}N_4$ requires C, 72·5; H, 4·8; N, 22·6%). The *dihydrochloride* crystallised from water as cubes, m. p. 330—333° (decomp.) (Found: N, 17·1; Cl, 21·7. $C_{15}H_{12}N_4,2HCl$ requires N, 17·4; Cl, 22·15%). Neither compound exhibited fluorescence.

NN'-Di-(2-hydroxyethyl)malonamide (5·7 g.) and *o*-phenylenediamine (5·4 g.) were refluxed together for 4 hr., then cooled. Addition of concentrated hydrochloric acid formed crystals, which, after recrystallisation (charcoal) from boiling water, melted at 329—333° (decomp.) and did not depress the m. p. of the hydrochloride obtained in the previous experiment.

Methylenebis-(5-*methyl*-2-*benziminazole*) *Dihydrochloride.*—Similarly prepared from malonamide and 3 : 4-diaminotoluene, this *salt* crystallised from aqueous hydrochloric acid in feathery needles, m. p. 332° (decomp.; inserted at 310°) (Found: N, 15·7; Cl, 19·7. $C_{17}H_{16}N_4,2HCl$ requires N, 16·05; Cl, 20·3%).

Tetramethylenebis-2-*benziminazole.*—*NN'*-Di-(2-hydroxyethyl)adipamide (11·6 g.) and *o*-phenylenediamine (5·4 g.) were refluxed together for 6 hr. The cooled mixture was extracted with boiling water. The residue (6·6 g.), recrystallised (charcoal) from aqueous ethanol, had m. p. 265—267° (Found: N, 19·1. Calc. for $C_{18}H_{18}N_4$: N, 19·3%). Shriner and Upson (*J. Amer. Chem. Soc.*, 1941, **63**, 2277) give m. p. 259—260°.

Octamethylenebis-2-*benziminazole.*—*NN'*-Di-(2-hydroxyethyl)sebacamide (10·0 g.) and *o*-phenylenediamine (5·5 g.) similarly gave this compound, m. p. 275° (Found: N, 15·7. Calc. for $C_{22}H_{26}N_4$: N, 16·2%). Shriner and Upson (*loc. cit.*) give m. p. 277—279°.

2-Phenylbenziminazole.—Ammonium benzoate (7·0 g.), *o*-phenylenediamine (5·5 g.), and glycerol (15 ml.) were refluxed for 3 hr. and poured into water. The precipitated solid (7·6 g.), recrystallised from ethanol, melted at 294° (Found : C, 80·0; H, 5·1. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·15%) (lit., m. p. 290°).

2-(2-Hydroxyphenyl)benziminazole.—Salicylamide (13·7 g.), *o*-phenylenediamine dihydrochloride (18 g.) and ethylene glycol (20 ml.) were refluxed for 4 hr., then poured into water, the suspension was neutralised with sodium hydrogen carbonate, and the solid was filtered off (11 g.). Recrystallisation (charcoal) from aqueous dioxan raised the m. p. to 241—242° (Found : C, 74·6; H, 4·5; N, 13·0. Calc. for $C_{13}H_{10}ON_2$: C, 74·4; H, 4·8; N, 13·3%). Walter and Freiser (*Analyt. Chem.*, 1953, **25**, 127) give m. p. 242°. The *hydrochloride*, recrystallised from water, had m. p. 254° (Found : N, 11·0; Cl, 14·55. $C_{13}H_{10}ON_2$,HCl requires N, 11·4; Cl, 14·4%).

2-(3-Hydroxy-2-naphthyl)benziminazole.—2-Hydroxy-3-naphthoic acid (9·4 g.), 2-hydroxyethylamine (10 g.), and *o*-phenylenediamine (5·4 g.) similarly formed the *naphthyl* compound, m. p. 298—300 (from 2-ethoxyethanol) (Found : C, 77·7; H, 4·7; N, 10·8. $C_{17}H_{12}ON_2$ requires C, 78·3; H, 4·6; N, 10·8%). This solid has a vivid orange fluorescence in ultra-violet light.

Benziminazole-2-carboxy-2'-hydroxyethylamide.—*NN'*-Di-(2-hydroxyethyl)oxamide (8·8 g.) and *o*-phenylenediamine (5·4 g.) were refluxed for 2 hr., then poured into water, and the yellow solid was filtered off. Recrystallisation (charcoal) from ethanol gave the benziminazole, m. p. 221° (Found : C, 58·2; N, 5·1; N, 20·0. Calc. for $C_{10}H_{11}O_2N_3$: C, 58·5; H, 5·4; N, 20·5%). Copeland and Day (*loc. cit.*) give m. p. 219—220°. Alcoholic solutions of this compound (and its 5-methyl homologue ; see below) were vividly fluorescent under ultra-violet light.

5-Methylbenziminazole-2-carboxy-2'-hydroxyethylamide.—Similarly prepared from 3 : 4-diaminotoluene and *NN'*-di-(2-hydroxyethyl)oxamide this *benziminazole* melted at 216° (Found : C, 60·0; H, 6·1; N, 18·8. $C_{11}H_{13}O_2N_3$ requires C, 60·3; H, 5·9; N, 19·2%).

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461. *The Degradation of Carbohydrates by Alkali. Part I. α-Alkoxy-ketones.*

By J. Kenner and G. N. Richards.

A study of the oxidation and hydrolysis of α-alkoxy-ketones under alkaline conditions leads to the conclusion that the former, but not the latter, is satisfactorily comparable with the behaviour of oxycelluloses.

One group, termed oxycelluloses, of the somewhat indefinite products resulting from the oxidation of cellulose is characterised by a pronounced liability to degradation by, for example, cold dilute sodium carbonate solution, and by reducing properties such as are usually regarded as typical of aldehydes. The latter might be attributable to the ·CH(OH)·CO· grouping which could well result from oxidation of cellulose. But depolymerisation by alkali must involve the glycoside linkages connecting the anhydroglucose units, and we are thus led to consider the behaviour of simple α-alkoxy-ketones. Their reducing properties have been repeatedly recorded (Grimaux and Lefevre, *Bull. Soc. chim.*, 1899, **1**, 12; Leonardi and de Franchis, *Gazzetta*, 1903, **33**, 319; Henry, *Compt. rend.*, 1904, **138**, 971; Gauthier, *Ann. Chim. Phys.*, 1909, **16**, 319), and the inference that these arise from a preliminary enolisation is supported by Hlasiwetz and Habermann's observation (*Annalen*, 1875, **246**, 340) that benzoquinone is formed when quinol monomethyl ether is boiled with ammoniacal silver nitrate; similarly, guaiacol exhibits reducing properties. Again, Irvine and Patterson surmised enolisation of 1 : 3 : 4 : 5-tetramethyl fructose from its degradation by cold alkaline potassium permanganate solution (*J.*, 1922, 2696).

A more detailed study of simple α-alkoxy-carbonyl compounds in this respect is therefore now presented. A comparative estimate of the extent of their enolisation in water

was obtained by direct titration against barium hydroxide (cf. Seidel, Thier, Uber, and Dittmer, *Ber.*, 1936, **69**, 650). The results (Table 1) illustrate the relative $-I$ effects of

TABLE 1. *Enolisation of substituted propan-2-ones in water (duplicate determinations).*

Propan-2-one derivative	Enolisation, %	Propan-2-one derivative	Enolisation, %
1-Methoxy-	1·12, 1·12	1 : 3-Diisopropoxy-	1·56, 1·57
1 : 3-Dimethoxy-	6·20, 6·18	1 : 3-Dibenzyloxy-	6·93, 7·00
1 : 3-Diethoxy-	2·82, 2·80	1-Hydroxy-3-methoxy-	3·41, 3·26
1 : 3-Di-*n*-propoxy-	2·13, 2·09	1 : 3-Dihydroxy-	0·09, 0·07
		Methoxyacetaldehyde	3·22, 3·14

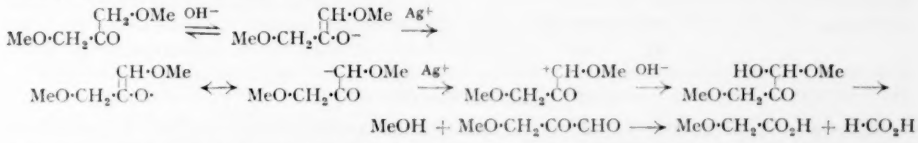
hydroxyl and alkoxyl groups in promoting the removal of proton requisite for enolisation, but it seems that symmetry also asserts itself as a factor in resonance.

Ultra-violet absorption measurements in this series indicated that enolisation occurred smoothly and rendered possible a determination of the time taken to attain equilibrium in 0·05N-sodium hydroxide (see Table 2).

TABLE 2. *Ultra-violet absorption of substituted propan-2-ones.*

Propan-2-one derivative	In water $\lambda_{max.}$, Å	In water ε	In 0·05N-NaOH, equil. state $\lambda_{max.}$, Å	In 0·05N-NaOH, equil. state ε	Time (hr.) reqd. for equil.
1-Methoxy-	2660	13·5	2530	39·2	>9
1 : 3-Dimethoxy-	2750	18·4	2490	156	5·0
1 : 3-Dihydroxy-	2700	22·5	2940	872	1·5
1-Hydroxy-3-methoxy-	2810	94·4	3060	452	1·0
Fructose	2780	0·6	2980	199	>9

With 1 : 3-dihydroxy- and 1-hydroxy-3-methoxy-propan-2-one, aldol condensation could follow enolisation and, in accord with this, an equilibrated solution of fructose in the same alkali showed a similar absorption spectrum. The same tendency to condensation limits the yield of each of the products of oxidation of 1 : 3-dimethoxypropan-2-one at the ordinary temperature by silver oxide in presence of sodium hydroxide to about 25% in each case, but the reaction proceeds smoothly and follows a course of which the following would appear a reasonable representation :



The second stage of the oxidation could clearly be achieved more directly with the aid of hydroxyl radicals available in alkaline potassium permanganate solution (Duke, *J. Amer. Chem. Soc.*, 1948, **70**, 3975), as used by Irvine and Patterson (*loc. cit.*). The limitation of acid yields by condensation is demonstrated by the results expressed in Tables 3 and 4,

TABLE 3. *Qualitative oxidations with silver oxide in* N*-sodium hydroxide.*

Compound	Products	Recovery (%)	Compound	Products	Recovery (%)
$MeO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OMe$	MeOH	26·8	$HO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OH$	$H{\cdot}CO_2H$	75·0
	$H{\cdot}CO_2H$	26·9		$HO{\cdot}CH_2{\cdot}CO_2H$	72·0
	$MeO{\cdot}CH_2{\cdot}CO_2H$	26·8			
$HO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OMe$	MeOH	49·8	$MeO{\cdot}CH_2{\cdot}CHO$	MeOH	7·4
	$H{\cdot}CO_2H$	24·9		$H{\cdot}CO_2H$	18·8
	$HO{\cdot}CH_2{\cdot}CO_2H$	27·5		$MeO{\cdot}CH_2{\cdot}CO_2H$	72·7
	$MeO{\cdot}CH_2{\cdot}CO_2H$	11·9			

TABLE 4. *Quantitative oxidations with silver oxide in* 0·1N*-sodium hydroxide.*

Compound	Equil. time (min.)	Yield of acids (equiv./mole)	Compound	Equil. time (min.)	Yield of acids (equiv./mole)
$MeO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OMe$	230	1·61	$HO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OH$	<5	2·03
$HO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OMe$	30	1·66	$MeO{\cdot}CH_2{\cdot}CHO$	<5	1·11

whence it is evident that if the oxidation proceeds rapidly little condensation occurs and the yields of acid approach the theoretical. For example, 1 : 3-dihydroxypropan-2-one is oxidised exothermally under the conditions described with the formation of approximately equivalent amounts of formic and glycollic acids. The yields are about three times as great as those obtained from 1 : 3-dimethoxypropan-2-one, oxidation of which under the same conditions required almost 4 hr.

The alternative modes of enolisation of 1-hydroxy-3-methoxypropan-2-one are reflected in two sets of oxidation products, in which glycollic is definitely preponderant over methoxyacetic acid :

$$HO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}OMe \begin{cases} \longrightarrow HO{\cdot}CH_2{\cdot}C(OH){:}CH{\cdot}OMe \longrightarrow HO{\cdot}CH_2{\cdot}CO_2H + H{\cdot}CO_2H + MeOH \\ \longrightarrow HO{\cdot}CH{:}C(OH){\cdot}CH_2{\cdot}OMe \longrightarrow MeO{\cdot}CH_2{\cdot}CO_2H + H{\cdot}CO_2H \end{cases}$$

Methoxyacetaldehyde also is evidently subject to enolisation since it furnished on oxidation almost 20% of formic acid together with 73% of methoxyacetic acid :

$$MeO{\cdot}CH_2{\cdot}CO_2H \longleftarrow MeO{\cdot}CH_2{\cdot}CHO \longrightarrow 2H{\cdot}CO_2H + MeOH$$

The α-alkoxy-carbonyl compounds were also found to undergo hydrolysis in boiling 0·5N-sodium hydroxide, with liberation of the corresponding alcohol identified in the form of its triphenylmethyl ether (cf. Table 6, p. 2244). As might be expected, much resinification occurred, apart from the hydrolysis. Furthermore, the latter does not at all correspond in facility with the degradation of oxycelluloses by weak alkali at the ordinary temperature, presumably because it involves the genesis of a doubly charged anion from a singly charged one :

$$-\overset{|}{C}(OR)=C(O^-)-O^- + OH^- \longrightarrow -C(CO^-)=C(O^-)-O^- + ROH$$

In subsequent papers of this series evidence will be adduced for the belief that the behaviour of oxycelluloses involves the transition from a singly charged anion to a neutral product by extrusion of anion from the β-position :

$$>\overset{|}{C}(XO)-\overset{|}{C}=C-O^- \longrightarrow >C=\overset{|}{C}-\overset{|}{C}=O + OX^-$$

Experimental

Materials.—1-Methoxypropan-2-one, prepared by the method of Gauthier (*loc. cit.*), exhibited the properties recorded by Mariella and Leech (*J. Amer. Chem. Soc.*, 1949, **71**, 3558).

1-Ethoxypropan-2-one, prepared from the corresponding secondary alcohol (compare Mariella and Leech, *loc. cit.*), exhibited the properties recorded by Henze and Rigler (*J. Amer. Chem. Soc.*, 1934, **56**, 1350) and was further characterised by its 2 : 4-*dinitrophenylhydrazone*, m. p. 160—161·5° (Found : C, 46·9; H, 5·0; N, 19·7. $C_{11}H_{14}O_5N_4$ requires C, 46·8; H, 5·0; N, 19·9%). The ketone gradually developed acidity, apparently owing to photo-oxidation.

1 : 3-*Dialkoxypropan-2-ones.*—Henze and Rogers' procedure (*J. Amer. Chem. Soc.*, 1939, **61**, 433) for the oxidation of 1 : 3-dimethoxypropan-2-ol furnished a product which, whilst being apparently homogeneous, gave only a 30% yield of the 2 : 4-dinitrophenylhydrazone. The following modification proved satisfactory : The alcohol (1 mole) was stirred with water (100 ml.) and sodium dichromate (1 mole) while concentrated sulphuric acid (195 ml.), diluted with water (400 ml.), was added at a rate sufficient to keep the mixture at 30—35° with the aid of cooling in ice-water. After 18 hr.' stirring at room temperature the solution was extracted with ether, and the extracts were shaken with anhydrous potassium carbonate until no longer acid. Since washing the ethereal solution with water entailed considerable loss of the ketone, the extract was shaken with an excess of anhydrous calcium sulphate for 1 hr., filtered, and fractionated. The ketones prepared in this way gave an almost theoretical yield of the corresponding 2 : 4-dinitrophenylhydrazones. Table 5 summarises the results.

The 2 : 4-*dinitrophenylhydrazones* of the following ketones were new (nos. as in Table 5) : (2), m. p. 85° (Found : C, 47·7; H, 5·5; N, 17·4. $C_{13}H_{18}O_6N_4$ requires C, 47·8; H, 5·6; N, 17·2%); (3), m. p. 39—39·5° (Found : C, 50·8; H, 6·3; N, 16·1. $C_{15}H_{22}O_6N_4$ requires C, 50·8; H,

6·3; N, 15·8%); (4), m. p. 77—78° (Found: C, 50·8; H, 6·4; N, 16·0%); (5), m. p. 87·5° (Found: C, 61·5; H, 4·9; N, 12·6. $C_{23}H_{22}O_6N_4$ requires C, 61·3; H, 4·9; N, 12·4%).

TABLE 5. *Substituted propan-2-ones.*

No.	Compound	B. p./mm.	n_D	Yield (%) (>90% purity)
1	1 : 3-Dimethoxypropan-2-one	71—71·5°/16	1·4189 (18°)	35·5
2	1 : 3-Diethoxypropan-2-one	90—92°/14	1·4192 (16°)	33·1
3	1 : 3-Di-*n*-propoxypropan-2-one	116—118°/21	1·4207 (25°)	43·0
4	1 : 3-Di*iso*propoxypropan-2-one	98—98·5°/13	1·4175 (22°)	34·0
5	1 : 3-Dibenzyloxypropan-2-one	208—212°/0·04	1·5483 (25°)	19·4

1 : 3-*Dibenzyloxypropan-2-one*, prepared according to the above procedure, suffers some oxidation during distillation, unless air is replaced by nitrogen (compare the case of dibenzyl ether, Eichel, U.S.P. 2,561,350) (Found: C, 75·6; H, 6·7. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%). The *semicarbazone* has m. p. 83° (Found: C, 66·2; H, 6·7; N, 13·0. $C_{18}H_{21}O_3N_3$ requires C, 66·0; H, 6·5; N, 12·8%).

1-*Hydroxy*-3-*methoxypropan*-2-*one*.—A solution of methoxyacetyl chloride (12 g.) in anhydrous ether (50 ml.) was gradually added to an ethereal solution (750 ml.) of diazomethane (10 g.) at 0°. After 20 hr. at the ordinary temperature and subsequent removal of solvent, sulphuric acid (0·5N; 50 ml.) was added to the residual yellow oil. The solution remaining after stirring of the mixture at the ordinary temperature until cessation of gas evolution (4 hr.) was saturated with sodium acetate and, after a further 20 hr.' storage, followed by exhaustive extraction with ether in the presence of barium carbonate, the extract was dried ($CaSO_4$). On distillation it furnished a fraction (3·1 g.; b. p. 40—85°/21 mm.) containing pyruvaldehyde, whose 2 : 4-dinitrophenylhydrazone, precipitated instantaneously at room temperature, showed m. p. and mixed m. p. 205°. 1-*Hydroxy*-3-*methoxypropan*-2-*one* (4·0 g., 35%) distilled at 89—90°/21 mm. and showed n_D^{23} 1·4507 (Found: C, 46·1; H, 7·5. $C_4H_8O_3$ requires C, 46·1; H, 7·7%). It reduced Fehling's solution and ammoniacal silver nitrate solution instantaneously at room temperature. The 2 : 4-dinitrophenylhydrazone had m. p. 175° (Found: N, 19·5; OMe, 10·7. Calc. for $C_{10}H_{12}O_6N_4$: N, 19·7; OMe, 10·9%) (Neuberg, *Biochem. Z.*, 1931, **238**, 459, and Fischer and Baer, *Ber.*, 1932, **65**, 345, found m. p. 175°).

Measurement of Enolisation (see Table 1).—A magnetically stirred solution of the carbonyl derivative (10^{-3} mole) in cold, boiled water (10 ml.) in a conical flask, closed by a stopper carrying a burette and a soda–lime tube, was titrated by dropwise addition of 0·01N-barium hydroxide until the phenolphthalein end-point persisted for at least 4 sec.

Ultra-violet Absorption (see Table 2).—Measurements were performed on solutions of each carbonyl derivative in 0·05N-sodium hydroxide solution (oxygen-free) in stoppered cells because an immediate decay in absorption followed access of air at any stage. In the first place a solution of the carbonyl derivative was examined after being left overnight to attain equilibrium; then solutions were examined at varying times after preparation to determine the period needed to attain constancy of absorption.

Oxidation of 1 : 3-*Dihydroxypropan*-2-*one and Related Compounds in Alkaline Solutions*.—1 : 3-*Dimethoxypropan*-2-*one*. (*a*) Quantitalive method (see Table 4). To a solution of the ketone (0·504 g.) in oxygen-free water (100 ml.) was added freshly precipitated, air-dried silver oxide (from 7·2 g. of silver nitrate), immediately followed by oxygen-free 0·2N-sodium hydroxide (100 ml.). The mixture was stirred vigorously at room temperature in nitrogen, whilst at intervals aliquot portions were withdrawn through a sintered-glass filter and run into an equal volume of 0·1N-sulphuric acid. The acid produced was titrated directly with sodium hydroxide solution. Equilibrium was attained smoothly in 230 min. at 20° and the final solution was yellow. The results of quantitative oxidations of this and of other ketones are summarised.

(*b*) Qualitative method (cf. Table 3). An aqueous solution (900 ml.) of the ketone (2·1 g.), freed from oxygen, was successively treated with freshly precipitated, well-washed silver oxide (from 30 g. of silver nitrate), and oxygen-free aq. N-sodium hydroxide (100 ml.). After agitation for 4 hr. in nitrogen at room temperature, the mixture was filtered into phosphoric acid (2M; 50 ml.). Methyl alcohol (with some formic acid) was removed by slow distillation, and identified by treatment of an aliquot portion with triphenylmethyl chloride in pyridine. The crude product was dried (P_2O_5) and extracted with a mixture of ether (15 ml.) and light petroleum (20 ml.; b. p. 60—80°), and the solution transferred to a column of alumina and eluted with light petroleum. Methyl triphenylmethyl ether, m. p. and mixed m. p. 82—83°, was then obtained in 26·8% yield. Formic acid was separated by repeated addition of water

and distillation of the acid liquor to dryness under reduced pressure and determined by reduction with mercuric oxide (Evans and Hass, *J. Amer. Chem. Soc.*, 1926, **48**, 2705). A small residual acidity in the distillate was due to methoxyacetic acid, of which the main proportion remained in the residue from the distillation. It was removed by extraction with ether, determined by titration (26·8% yield), and identified as the 4-*bromophenacyl* ester, plates, m. p. and mixed m. p. 76—77° (Found: C, 46·0; H, 3·8; OMe, 10·6. $C_{11}H_{11}O_4Br$ requires C, 46·0; H, 3·9; OMe, 10·8%).

1-*Hydroxy*-3-*methoxypropan*-2-*one*. Oxidation of this ketone as described above was complete in 30 min. (cf. Table 3). Methanol was identified as the triphenylmethyl ether. Formic acid in the acidic distillate was accompanied by a larger proportion of other acid than in the previous case. From this, after removal of formic acid, 4-bromophenacyl glycollate, m. p. and mixed m. p. 137—139°, was prepared and purified by repeated crystallisation from aqueous alcohol. Glycollic and methoxyacetic acids were also separated by paper chromatography of their sodium salts (Brown, *Biochem. J.*, 1950, **47**, 598). The respective R_F values were 0·085 and 0·164 (for $H{\cdot}CO_2^-$, 0·14), with butanol (4 vol.), 3N-ammonia (5 vol.), and ethanol (1 vol.) as eluant, the papers being eluted for several days at room temperature. The yields cited were based on determination of the methoxyl contents of salts and total acidity.

1 : 3-*Dihydroxypropan*-2-*one*. Formic acid was removed in steam but was accompanied by a small proportion of glycollic acid. The main proportion of the latter, remaining in the residue from the distillation, was extracted by ether and identified chromatographically and by conversion into its 4-bromophenacyl ester.

Methoxyacetaldehyde. Methoxyacetic acid, formic acid, and methyl alcohol were identified and estimated as above.

Action of Alkali on α-Alkoxy-carbonyl Derivatives.—Solutions of the ketones (*ca.* 5 g.) in oxygen-free 0·5N-sodium hydroxide (90 ml.) were heated in a slow stream of nitrogen for 1 hr. at 100°, 3·5 hr. at 105°, and 0·5 hr. at 110°, so that any distillate could be collected. After removal of any ketone as 2 : 4-dinitrophenylhydrazone, the distillate was redistilled and made up to 25 ml. for determination of its density, and hence its content of methyl or ether alcohol. The presence of this was confirmed by preparation of the corresponding triphenylmethyl ether, m. p. and mixed m. p. 82—83° or 83·5—84·5° respectively. The results obtained are in Table 6. Other products were not determined because the conditions employed obviously favoured extensive condensation and resinification occurred.

TABLE 6.

Propan-2-one derivative	Heating conditions	Yield of alcohol (%)
1 : 3-Dimethoxy-	As described above	50
1 : 3-Diethoxy-	,, ,,	26
1 : 3-Di-*n*-propoxy-	,, ,,	9
1-Hydroxy-3-methoxy-	,, ,,	49
1-Ethoxy-	Refluxing for 5 hr. and subsequent distilln.	16
Methoxyacetaldehyde	Refluxing for 1 hr. and subsequent distilln.	78

The work in this and the following paper forms part of a programme of fundamental research of the British Rayon Research Association.

THE BRITISH RAYON RESEARCH ASSOCIATION, BARTON DOCK ROAD,
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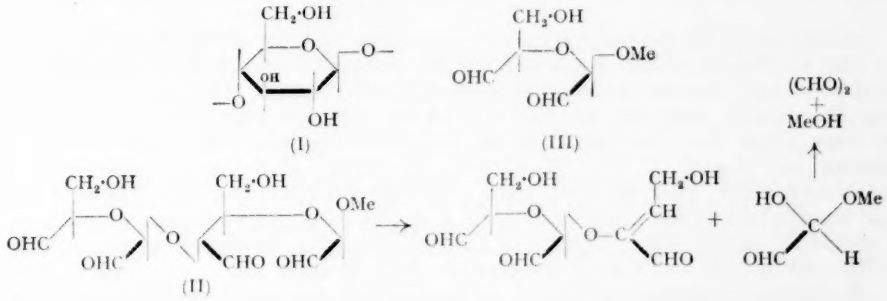
462. *The Degradation of Carbohydrates by Alkali. Part II.* Lactose.*

By W. M. Corbett and J. Kenner.

The decomposition by oxygen-free saturated lime-water at 25° of lactose into galactose and α- and β-*iso*saccharinic acids has been studied. Its mechanism is interpreted in terms of the behaviour of β-alkoxy-carbonyl compounds.

It was concluded in Part I * that analogy with α-alkoxy-ketones suffices to explain the reducing properties of many forms of oxycelluloses but not their sensitivity at the ordinary temperature to weak alkali. Now, in an anhydroglucose unit (I) of cellulose replacement of any of the alcohol groups by a carbonyl group leads to a structure which in relation to the adjoining anhydroglucose units of the chain can be regarded not only as an α- but also as a β-alkoxycarbonyl compound, and in this and subsequent papers we shall adduce evidence of the merits of the latter comparison. Although the behaviour of β-alkoxycarbonyl derivatives towards alkali has not been systematically studied, the formation of αβ-unsaturated carbonyl systems from β-hydroxy- and β-nitrosamino-carbonyl derivatives (Jones and Kenner, *J.*, 1933, 363, Adamson and Kenner, *J.*, 1934, 838), and the reversal of the Michael reaction (Ingold and Powell, *J.*, 1921, 1976) are familiar. Closer to our theme is the formation of tetraethyl propane-1 : 1 : 3 : 3-tetracarboxylate by interaction of chlorodimethyl ether with ethyl sodiomalonate (Simonsen, *J.*, 1908, **93**, 1777) and of crotononitrile by the action of ethylmagnesium iodide on β-methoxybutyronitrile (Bruylants and Mathus, *Bull. Acad. roy. Belg.*, 1926, **11**, 637), and Head has recorded the rapid formation of glyoxal by the action of cold dilute aqueous sodium carbonate on the periodate oxidation product (II) of β-methylcellobioside but not from that of β-methylglucoside (III) (*J. Textile Inst.*, 1947, **38**, 389) :

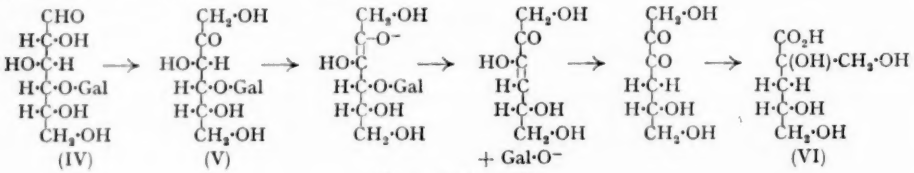


Owing to the indefinite character of the oxycelluloses we have in mind (to which we assign the generic term " carbonyl oxycelluloses ") we have first studied lactose from this point of view. Lactose was dissolved in oxygen-free saturated lime-water solution at 25° and at appropriate intervals the changes in alkalinity, optical rotatory power, and contents of mono- + di-saccharide, monosaccharide, and saccharinic acid were determined, the identity of the monosaccharides being established by paper chromatography. The results exhibited in the accompanying Table show a correspondence between the rate of decomposition of lactose and the rates of formation of monosaccharides and saccharinic acids.

The known relatively slow conversion of lactose (IV) into lactulose (V) (Montgomery and Hudson, *J. Amer. Chem. Soc.*, 1930, **52**, 2101) is followed by the rapid degradation of

* Part I, preceding paper.

the latter into α- and β-*iso*saccharinic acids (VI) and galactose, the latter being in turn gradually disintegrated into acidic products :



(Gal = galactosyl)

Degradation of lactose by saturated lime-water at 25°.

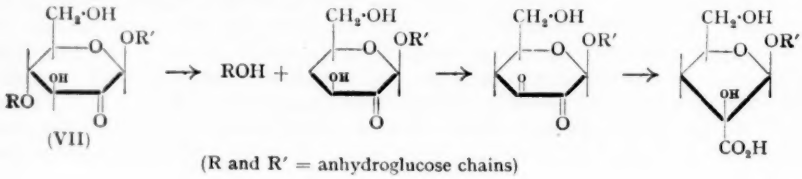
Time (hr.)	α_D	Lactose present	(10^{-4} mole) decompd.	De-comp. (%)	Monoses (10^{-4} mole)	Sac-charinic acids (10^{-4} mole)	Paper chromatography † Lact-ose	Lac-tulose	Gal-actose	Tag-atose	Sac. acids	Tal-ose
0·1	+0·20°	1·042	0	0	0	*	4	—	—	—	—	—
0·5	0·20	1·022	0·020	1·9	0·042	*	4	1	—	—	—	—
1	0·20	1·018	0·024	2·4	0·055	*	4	1	—	—	—	—
2	0·18	0·972	0·070	6·7	0·132	*	4	2	—	—	—	—
3	0·16	0·968	0·074	7·2	0·160	*	4	2	1	—	—	—
4	0·14	0·965	0·077	7·4	0·168	*	4	2	1	—	—	—
6	0·10	0·935	0·107	10·3	0·172	*	4	2	1	—	—	—
7	0·12	0·895	0·147	14·2	0·250	0·138	4	2	1	—	—	—
24	0·05	0·685	0·357	33·9	0·395	0·422	3	3	2	1	1	—
31	0·04	0·592	0·450	43·2	0·480	0·452	3	3	2	1	1	1
48	0·05	0·402	0·640	61·4	0·660	0·532	3	3	2	1	2	1
55	0·05	0·355	0·687	66·0	0·722	0·680	3	3	2	1	2	1
72	0·05	0·272	0·770	73·9	0·758	0·745	2	3	2	1	2	1
96	0·05	0·226	0·816	78·2	0·792	0·752	2	3	2	1	2	1
122	0·05	0·175	0·867	83·3	0·820	0·758	1	3	2	1	3	1
168	0·05	0·168	0·874	84·0	0·777	*	1	3	2	1	3	1
216	0·05	0·146	0·896	85·8	0·758	0·832	1	3	1	1	3	1

* Not determined. † Numerals denote relative intensity, 4 denoting the greatest intensity.

In later papers the general applicability of the above scheme will be illustrated.

The significance of the β-hydroxycarbonyl system for carbohydrate chemistry has been previously discussed by Wohl (*Z. angew. Chem.*, 1907, **20**, 1169) and Isbell (*J. Res. Nat. Bur. Stand.*, 1944, **32**, 45), and that of the β-alkoxycarbonyl system by Nicolet (*J. Amer. Chem. Soc.*, 1931, **53**, 4458) and, with particular reference to oxycelluloses, by Haskins and Hogsed (*J. Org. Chem.*, 1950, **15**, 1264). Much earlier Kiliani and his collaborators (*Ber.*, 1909, **42**, 2603, 3903, and earlier papers) had obtained *iso*saccharinic acid from lactose by the action of lime-water at and above room temperature. Further, it should be realised that acceptance of the mechanism here developed involves rejection of that put forward by Evans (*Chem. Reviews*, 1942, **31**, 537).

Meanwhile, it appears permissible to interpret the decomposition of carbonyl oxycelluloses along similar lines. Thus, in the case of a 2-carbonyl group in an anhydroglucose unit (VII) of the cellulose chain we have :



(R and R′ = anhydroglucose chains)

Experimental

Determination of the Degradation Products.—A solution (100 ml.) of "AnalaR" lactose (0·8675 g.) in saturated oxygen-free lime-water (0·0386N) was kept at 25°. At intervals

5-ml. portions, again freed from oxygen by a stream of oxygen-free nitrogen, were titrated against 0·02N-sulphuric acid (bromothymol-blue), and diluted to 20 ml. The optical rotatory power was observed and an indication of the sugars present was obtained by paper chromatographic analysis. The saccharinic acid content of this solution (1 ml.) was determined by the lactonisation method of Bamford, Bamford, and Collins (*Proc. Roy. Soc.*, 1950, *A*, **204**, 85).

For determination of the saccharides the solution (2 ml.) was diluted to 25 ml. and the adsorbate on a charcoal–Celite column (0·8 × 1·0 cm.) from an aliquot portion (1 ml.) of this diluted solution was eluted with water (15 ml.), the monose content of the eluate being determined by Hagedorn and Jensen's micro-method (*Biochem. Z.*, 1923, **135**, 46). The difference in reducing power of the solution before and after adsorption on the charcoal column was due to the disaccharides only.

The results recorded in the table are calculated for the solution used for the observation of α_D; although a complex mixture of carbohydrates may arise in solution, *e.g.*, by epimerisation, the total monosaccharides are quoted as galactose and the total disaccharides as lactose rather than as individual components.

Isolation of the Degradation Products. Lactose (8·599 g.) was dissolved in saturated oxygen-free lime-water (1 l.) and kept at 25° for 10 days, after which the solution was neutralised with oxalic acid. The filtered solution was concentrated to 50 ml. at 45° under reduced pressure. Calcium α-*iso*saccharinate (1·635 g.) slowly crystallised. The brucine salt (m. p. 159—161°) was prepared by the standard method (Found: N, 5·1. Calc. for $C_{29}H_{38}O_{10}N_2$: N, 4·9%). Nef (*Annalen*, 1910, **376**, 52) gives m. p. 164°. The mother-liquors were concentrated to a syrup which slowly crystallised, to give galactose (0·676 g.), $[\alpha]_D^{23}$ (equil.) +76·5° (*c*, 0·890 in H_2O) [osazone, m. p. 194·5—196° (decomp.); Fischer (*Ber.*, 1887, **20**, 3390) gives m. p. 196—197°]. From a portion of the residual syrup (0·429 g.) was isolated the brucine salt of β-*iso*saccharinic acid (0·144 g.), m. p. 185—209° (decomp.) (Found: N, 5·3%). Nef (*loc. cit.*) gives m. p. 200—210° (decomp.).

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463. *A Convenient Synthesis of* bicyclo[5 : 3 : 0]*Dec*-1(7)-*en*-8-*one and Related Compounds.*

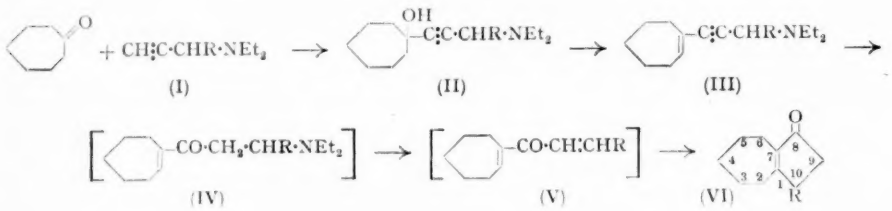
By A. M. ISLAM and R. A. RAPHAEL.

Cyclisation of the readily prepared 1-(3-diethylaminoprop-1-ynyl)*cyclo*heptan-1-ol (II; R = H) by a hot mixture of phosphoric and formic acids containing mercuric acetate leads directly to *bicyclo*[5 : 3 : 0]dec-1(7)-en-8-one (VI; R = H). Application of the reaction to other allied bicyclic systems is described.

IN recent years a series of memoirs by Nazarov and his co-workers (*inter al.*, *J. Gen. Chem. Russia*, 1950, **20**, 1431 *et seq.*, 2009, 2079, 2091, and earlier papers) has described the acid-induced cyclisation of a wide variety of allyl vinyl and divinyl ketones to substituted *cyclo*pentenones, the most general procedure involving treatment with a hot mixture of phosphoric and formic acids; the mechanism of the reaction has been discussed by Braude and Coles (*J.*, 1952, 1430). The wide applicability of the reaction suggested its extension to compounds of the *bicyclo*[5 : 3 : 0]decane system, the difficult accessibility of which has hampered the study of their dehydrogenation products, the azulenes. This approach has indeed already been envisaged by Braude and Forbes (*Nature*, 1951, **168**, 874) who developed a five-stage process for the conversion of *cyclo*heptanone into *bicyclo*[5 : 3 : 0]dec-1(7)-en-8-one. While presenting several novel features the route involved is rather lengthy and is not readily adaptable to large-scale working. A new approach to the problem was suggested by the recent availability of acetylenic amines of the general type (I) which are

obtained from acetylene by the Mannich reaction (Copenhaver and Bigelow, " Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, 1949, p. 110). By their use a convenient two-stage conversion of *cyclo*heptanone into *bicyclo*[5 : 3 : 0]dec-1(7)-en-8-one (VI; R = H) has been achieved.

A condensation in liquid ammonia between *cyclo*heptanone and the lithium salt of 3-diethylaminoprop-1-yne (prepared *in situ* by treating 2-bromo-3-diethylaminoprop-1-ene with two mols. of lithamide) gave the corresponding acetylenic alcohol (II; R = H). Heating this compound with phosphoric–formic acid yielded mainly the dehydration product (III; R = H), but when the process was repeated in the presence of a small quantity of mercuric acetate conversion into the bicyclic ketone (VI; R = H) ensued. The identity of the material was confirmed by a mixed melting point of its semicarbazone



with an authentic specimen (we are indebted to Professor J. W. Cook, F.R.S., for kindly providing a sample). The rationale of this cyclisation may be envisaged as follows. The initial formation of the dehydration product (III; R = H) is followed by hydration of the triple bond to form the unsaturated diethylamino-ketone (IV; R = H). The mode of addition leading to this vinyl ketone rather than to the isomeric allyl ketone may be confidently predicted from the results of Hamlet, Henbest, and Jones (*J.*, 1951, 2652) on the hydration of substituted vinylacetylenes; in this case the polarisation $\overset{\delta+}{\cdot}C\equiv\overset{\delta-}{C}\cdot CH_2\cdot\overset{+}{N}HEt_2$ would be further favoured by the juxtaposition of the strongly electron-attracting tertiary ammonium cation (for convenience the above flow sheet shows the compounds as free bases rather than salts). The position of the diethylamino-group in (IV) β to the carbonyl group favours the ready elimination of diethylamine (cf. the production of vinyl ketones from salts of Mannich bases; Mannich *et al.*, *Ber.*, 1941, **74**, 554; 1922, **55**, 356, 3504; *Arch. Pharm.*, 1927, **265**, 598) with the production of the divinyl ketone (V; R = H); Nazarov cyclisation of (V) then leads to the bicyclic product (VI). Although the conversion of *cyclo*heptanone into bicyclic ketone is small (26% allowing for recovered ketone; 15% overall) the method is rapid and simple and its attractiveness is enhanced by the ease of separation of the neutral product from any unchanged basic intermediates.

Extension of the synthesis to the homologous 3-diethylaminobut-1-yne (I; R = Me) gave the corresponding acetylenic alcohol (II; R = Me). The presence of the methyl group in this compound greatly facilitated its Nazarov cyclisation to (VI; R = Me), the conversion proceeding smoothly in the absence of mercuric salt. Application of the procedures to *cyclo*hexanone yielded **4 : 5 : 6 : 7**-tetrahydroindanone and its 3-methyl homologue. The former product was also obtainable by the Nazarov cyclisation of 1-(3-hydroxyprop-1-ynyl)*cyclo*hexan-1-ol, prepared in low yield from *cyclo*hexanone and propargyl alcohol (Zeile and Meyer, *Ber.*, 1942, **75**, 356). Condensation of the lithium salt of 3-diethylaminoprop-1-yne with *cyclo*pentanone gave disappointing yields, much *cyclo*pentylidene*cyclo*pentanone being produced. However, the required material was obtained by subjecting 1-acetoxy-1-ethynyl*cyclo*pentane to the Mannich reaction with formaldehyde and diethylamine (Jones, Marszak, and Bader, *J.*, 1947, 1578). Nazarov cyclisation of the resulting 1-acetoxy-1-(3-diethylaminoprop-1-ynyl)*cyclo*pentane did furnish the expected *bicyclo*[3 : 3 : 0]oct-1(5)-en-2-one, but much tar was simultaneously produced and the yield was correspondingly low.

Experimental

In all experiments the concentration of formic acid was 90% and that of phosphoric acid 85%. All 2 : 4-dinitrophenylhydrazones were purified by chromatography (benzene–alumina) and crystallised from ethyl acetate–alcohol.

1-(3-*Diethylaminoprop*-1-*ynyl*)cyclo*heptan*-1-*ol* (II; R = H).—To a solution of lithamide (formed from lithium, 2·2 g., by the catalytic action of ferric nitrate) in liquid ammonia (400 c.c.) was added 2-bromo-3-diethylaminoprop-1-ene (30 g.) (Parcell and Pollard, *J. Amer. Chem. Soc.*, 1950, **72**, 2385), and the mixture stirred for 4 hr. A solution of *cyclo*heptanone (11·2 g.) in dry ether (15 c.c.) was then added dropwise during 30 min. and the stirring continued for a further 4 hr. After introduction of powdered ammonium chloride (10 g.) the ammonia was allowed to evaporate off and the residue treated with 2N-sulphuric acid and ether. The aqueous layer was then further extracted with ether; drying, evaporation, and distillation of the combined ethereal extracts gave unchanged *cyclo*heptanone (4·2 g.). Basification of the aqueous layer and isolation by means of ether gave 1-(3-*diethylaminoprop*-1-*ynyl*)cyclo*heptan*-1-*ol* (9·9 g., 72% based on reacted ketone) as a viscous oil, b. p. 102°/0·3 mm., n_D^{19} 1·4985 (Found: N, 6·4. $C_{14}H_{25}ON$ requires N, 6·3%).

bicyclo[5 : 3 : 0]*Dec*-1(7)-*en*-8-*one* (VI; R = H).—A mixture of the above acetylenic alcohol (4·4 g.), formic acid (12 g.), and phosphoric acid (3·5 g.) was boiled under gentle reflux for 6 hr. Water was then added and the precipitated oil extracted with ether. Washing (sodium carbonate solution), drying (Na_2SO_4), evaporation of the extract, and distillation of the residue gave the bicyclic ketone (VI; R = H) (0·25 g., 8%) b. p. 73°/0·2 mm., n_D^{18} 1·5241. The purified semicarbazone had m. p. 236° undepressed by an authentic sample (Cook, Philip, and Somerville, *J.*, 1948, 164, give b. p. 58—60°/0·1 mm., $n_D^{11\cdot5}$ 1·5275, and semicarbazone m. p. 235—236°). The 2 : 4-*dinitrophenylhydrazone* crystallised as red needles, m. p. 230° (Found: C, 58·2; H, 5·2; N, 17·1. $C_{16}H_{18}O_4N_4$ requires C, 58·1; H, 5·4; N, 16·95%).

Neutralisation of the aqueous layer with ammonia and isolation by means of ether gave 1-(3-*diethylaminoprop*-1-*ynyl*)cyclo*hept*-1-*ene* (III; R = H) (3·2 g., 80%) as a colourless mobile oil, b. p. 88°/0·2 mm., n_D^{17} 1·5088 (Found: N, 6·7. $C_{14}H_{23}N$ requires 6·8%).

When mercuric acetate (0·5 g.) was added after the above reflux period and the heating continued for a further 4 hr. isolation as above gave a greatly enhanced yield (35%) of the bicyclic ketone. Subjection of (III; R = H) to this procedure gave a similar yield of the ketone.

1-(3-*Diethylaminobut*-1-*ynyl*)cyclo*heptan*-1-*ol* (II; R = Me).—To a solution of lithamide (from lithium, 1·7 g.) in liquid ammonia (400 c.c.) was added 3-diethylaminobut-1-yne (I; R = Me) (28 g.), and the mixture stirred for 1 hr. *cyclo*Heptanone (20 g.) in an equal volume of dry ether was then added and the stirring was continued for a further 4 hr. After addition of ammonium chloride (10 g.) and evaporation of the ammonia, the residue was treated with excess of 2N-sulphuric acid, and the non-basic constituents were extracted with ether; from this extract unchanged *cyclo*heptanone (11·5 g.) was recovered. The aqueous layer was basified with concentrated aqueous ammonia, and the precipitated oil isolated by ether; distillation gave 1-(3-*diethylaminobut*-1-*ynyl*)cyclo*heptan*-1-*ol* (13·5 g., 80% based on ketone which reacted), b. p. 104°/0·5 mm., n_D^{15} 1·4962 (Found: N, 6·1. $C_{15}H_{27}ON$ requires N, 5·9%). Employment of the Grignard derivative of the acetylenic amine in this condensation gave a much lower yield (35%) of the required product and very little *cyclo*heptanone was recovered.

10-*Methyl*bicyclo[5 : 3 : 0]*dec*-1(7)-*en*-8-*one* (VI; R = Me).—The above acetylenic alcohol (II; R = Me) (5 g.) was heated under reflux with formic acid (10 g.) and phosphoric acid (3·5 g.) for 4 hr. Working up as in the above cognate preparation gave 10-methyl*bicyclo*-[5 : 3 : 0]dec-1(7)-en-8-one (1·2 g., 35%), b. p. 140°/15 mm., n_D^{20} 1·5138; the 2 : 4-dinitrophenylhydrazone formed red needles, m. p. 236°, undepressed on admixture with an authentic sample (Braude and Forbes, *loc. cit.*, give n_D^{23} 1·5118 and 2 : 4-dinitrophenylhydrazone, m. p. 236°).

4 : 5 : 6 : 7-*Tetrahydroindan*-1-*one*.—(*a*) Treatment as in the above cognate preparation of lithamide (from lithium, 2·2 g.) in liquid ammonia (400 c.c.) with 2-bromo-3-diethylaminoprop-1-ene (30 g.), followed by addition of *cyclo*hexanone (14 g.), gave 1-(3-*diethylaminoprop*-1-*ynyl*)-cyclo*hexan*-1-*ol* (13 g.) as a viscous oil, b. p. 84°/0·2 mm., n_D^{19} 1·4959 (Found: N, 7·0. $C_{13}H_{23}ON$ requires N, 6·7%). This product (4 g.) was heated under reflux for 4 hr. with formic acid (10 g.) and phosphoric acid (3 g.); mercuric acetate (0·5 g.) was then added and the heating continued for a further 4 hr. Working up in the usual manner gave 4 : 5 : 6 : 7-tetrahydroindanone (1 g., 52%), b. p. 154°/16 mm., n_D^{16} 1·5022 [2 : 4-dinitrophenylhydrazone, m. p. 238° undepressed by an authentic specimen (Mathieson, *J.*, 1951, 177 gives m. p. 238°)]. If the mercuric acetate

treatment was omitted only a trace of ketonic material was formed, the product (90% yield) consisting of 1-(3-*diethylaminoprop*-1-*ynyl*)cyclo*hex*-1-*ene*, b. p. 78°/0·2 mm., n_D^{18} 1·5001; light absorption in EtOH: $\lambda_{max.}$ 2300 Å (ε = 9500) (Found: N, 6·9. $C_{13}H_{21}N$ requires N, 7·3%). Application of the mercuric acetate treatment to this converted it into tetrahydroindanone (48%). (*b*) When 1-(3-hydroxyprop-1-ynyl)*cyclo*hexan-1-ol (5 g.) prepared by the procedure of Zeile and Meyer (*loc. cit.*) was heated for 4 hr. with formic acid (10 g.) and phosphoric acid (2 g.) there was isolated the same tetrahydroindanone (2·2 g., 50%).

3-*Methyl*-4 : 5 : 6 : 7-*tetrahydroindan*-1-*one*.—By interaction of lithamide (from lithium, 1·5 g.), 3-diethylaminobut-1-yne (25 g.), and *cyclo*hexanone (20 g.) as in the above cognate preparation, there was obtained 1-(3-*diethylaminobut*-1-*ynyl*)cyclo*hexan*-1-*ol* (25 g.) as a viscous oil, b. p. 100°/0·6 mm., n_D^{21} 1·4910 (Found: N, 5·85. $C_{14}H_{25}ON$ requires N, 6·2%). Heating a mixture of this (4 g.), formic acid (10 g.), and phosphoric acid (3·5 g.) for 6 hr. furnished 3-methyl-4 : 5 : 6 : 7-tetrahydroindan-1-one (1·4 g., 51%), b. p. 135°/16 mm., n_D^{19} 1·5116; the 2 : 4-dinitrophenylhydrazone formed red needles, m. p. 242° undepressed by an authentic sample (Hamlet, Henbest, and Jones, *loc. cit.*, give n_D^{15} 1·5135, and 2 : 4-dinitrophenylhydrazone, m. p. 246°).

bicyclo[3 : 3 : 0]*Oct*-1(5)-*en*-2-*one*.—On being heated with four times its volume of acetic anhydride for 2 hr. 1-ethynyl*cyclo*pentan-1-ol was converted into its *acetate* (86% yield), b. p. 68°/15 mm., n_D^{16} 1·4595 (Found: C, 70·75; H, 7·2. $C_9H_{12}O_2$ requires C, 71·0; H, 7·8%). The acetate (8·5 g.), diethylamine (4 g.), paraformaldehyde (2·2 g.), and dioxan (10 c.c.) were heated by steam for 3 hr., then set aside overnight. Dilute hydrochloric acid was added and the neutral constituents were extracted with ether. Basification of the aqueous layer with sodium hydroxide solution followed by isolation by means of ether gave 1-*acetoxy*-1-(3-*diethylamino*-*prop*-1-*ynyl*)cyclo*pentane* (11 g., 83%), b. p. 76°/0·2 mm., n_D^{18} 1·4722 (Found: N, 5·75. $C_{14}H_{23}O_2N$ requires N, 5·9%). This product (8 g.) was heated under reflux for 5 hr. with formic acid (15 g.) and phosphoric acid (3 g.); the mixture rapidly darkened. Working up as in the cognate experiments gave *bicyclo*[3 : 3 : 0]oct-1(5)-en-2-one (0·3 g., 7%), b. p. 122°/15 mm., n_D^{21} 1·5226 (Cope and Schmitz, *J. Amer. Chem. Soc.*, 1950, **72**, 15 give n_D^{25} 1·5202). The semicarbazone of this product melted unsharply at *ca.* 205° (Cope and Schmitz, *loc. cit.*, give m. p. 230—232·2°) even after repeated crystallisation; this suggests contamination of the product with the uncyclised divinyl ketone. The 2 : 4-*dinitrophenylhydrazone* was readily purified, however, and crystallised in red needles, m. p. 196°; light absorption in EtOH: $\lambda_{max.}$ 3800 (ε = 27,500) and 2550 Å (ε = 16,500) (Found: N, 18·75. $C_{14}H_{14}O_4N_4$ requires N, 18·5%). Neutralisation of the acid aqueous layer gave 1-(3-*diethylaminoprop*-1-*ynyl*)cyclo*pent*-1-*ene* (5 g., 87%) b. p. 57°/0·2 mm., n_D^{16} 1·4995 (Found: N, 7·95. $C_{12}H_{19}N$ requires N, 7·9%). Cyclisation of this enyne by the mercuric acetate technique gave a similar yield (6%) of *bicyclo*[3 : 3 : 0]octenone.

We thank Professor J. W. Cook, F.R.S., for his interest. Gratitude is also expressed to Dr. E. A. Braude, Dr. H. B. Henbest, and Dr. D. W. Mathieson for specimens and to Imperial Chemical Industries Limited, Dyestuffs Division, for a generous gift of diethylaminobutyne.

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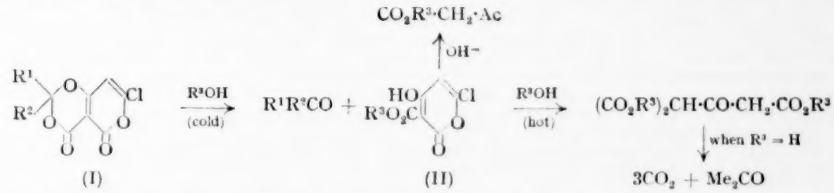
464. ***Heterocyclic Syntheses with Malonyl Chloride. Part II.**** **2 : 2-*Disubstituted 6′-Amino-2′ : 4-diketopyrano(3′ : 4′-5 : 6)-1 : 3-dioxins and Simpler Derivatives of 4-Keto-1 : 3-dioxin.***

By S. J. Davis and J. A. Elvidge.

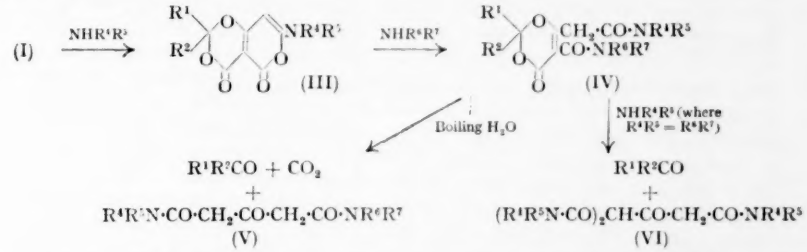
The chloropyronodioxins (I), prepared from malonyl chloride and ketones, react stepwise with primary and secondary amines to yield (non-basic) aminopyronodioxins (III) and thence, with fission of the pyrone ring, biscarboxyamide derivatives (IV) of 4-keto-1 : 3-dioxin. The unsaturated lactone-like ring of these compounds is stable to acid but not basic reagents. Sodium hydroxide or boiling water degrades the ketodioxins (IV) to acetone 1 : 3-dicarboxyamides, whilst amines yield acetone-1 : 1 : 3-tricarboxyamides; sodium methoxide with the dianilide (IV) afforded a monoester dianilide of acetone-tricarboxylic acid.

Light absorptions are recorded for the new heterocyclic series (III) and (IV).

6′-Chloro-2′ : 4-diketopyrano(3′ : 4′-5 : 6)-1 : 3-dioxin derivatives (I), which are formed by heating malonyl chloride with ketones, interact readily with alcohols and water (Part I*), according to the scheme :



We have now examined the behaviour of compounds (I) towards primary and secondary amines. End-products analogous to the above are given, *viz.*, acetone-1 : 1 : 3-tricarboxyamides (VI) and the original ketone, but the intermediate reaction stages are different. First there is replacement of the chlorine atom then fission of the pyrone ring, and *lastly* fission of the ketodioxin ring :



The stages are clear-cut, and the products (III), (IV), (V), and (VI) are obtained in good yields.

6′-Amino-2 : 4′-diketopyrano(3′ : 4′-5 : 6)-1 : 3-dioxins.—Treatment of the chloropyronodioxins (I), $C_7HR^1R^2O_5Cl$, in chloroform with 2 mols. of various amines (NHR^4R^5) gave amine hydrochlorides and the 6′-substitution products (III), $C_7HR^1R^2O_5NR^4R^5$, which are listed in Table 1. These aminopyranodioxins absorbed light strongly in the 3300—3400-Å region and resembled in this respect the simpler pyrone derivative (VII), obtained from (II; R^3 = Et) with morpholine.

The aminopyronodioxins (III), unlike the parent chloro-compounds (I), were stable to water and alcohols. They lacked basic properties, simulating amides. In particular

* Part I, *J.*, 1952, 4109.

TABLE 1. *6′-Amino-2′ : 4-diketopyrano(3′ : 4′-5 : 6)-1 : 3-dioxins* (III) *and a related pyran.*

Chloro-compound (I)					Product (III)	Yield	
No.	R^1, R^2	(g.)	Base, c.c.	Method *	NR^4R^5	(%)	Form, solvent †
1	Me_2	0·5	Morpholine, 0·38	*a*	Morpholino	93	Needles, EtOH
2	,,	4·61	Piperidine, 3·95	,,	Piperidino	72	Needles, C_6H_6–Pet
3	,,	2·3	$NHEt_2$, 2·06	,,	NEt_2	91	Prisms, EtOH
4	,,	0·46	NHMePh, 0·435	,,	NMePh	73	Needles, EtOH
5	,,	5	NH_2Ph, 4	*b*	NHPh	98	EtOH
6	,,	4·61	$NH_2{\cdot}CH_2Ph$, 4·36	,,	$NH{\cdot}CH_2Ph$	98	EtOH
7	,,	2·04	Aq. NH_3 (*d* 0·88), 1·1	*c*	NH_2 [1]	38	EtOH
8	Ph_2	0·5	Morpholine, 0·5	*d* [2]	Morpholino	70	Plates, $CHCl_3$–Et_2O
9	,,	3·55	Piperidine, 2·05	*d*	Piperidino	70	Leaflets, *cyclo*hexanone
10	,,	3·55	NH_2Bu^n, 2	*a*	$NHBu^n$	85	Prisms, EtOH
11	,,	5	$NH_2{\cdot}CH_2Ph$, 3·08	,,	$NH{\cdot}CH_2Ph$	66	Needles, $H{\cdot}CO{\cdot}NMe_2$–EtOH
12	,,	5	NH_2Ph, 2·54	,,	NHPh	85	,, ,,
13	Me, Pr^n	1	Morpholine, 0·67	*a* [3]	Morpholino	66	C_6H_6–Pet
14	Me, Ph	1	,, 0·59	*a*	,,	51	Pr^nNO_2
15	Me, CO_2Et	0·98	$NHEt_2$, 0·7	*a* [2]	NEt_2	49	Needles, EtOH
16	$\cdot[CH_2]_5\cdot$	0·5	Morpholine, 0·32	*a* [2]	Morpholino	56	C_6H_6
17	Chloro-compound (II), R^3 = Et	0·33	Morpholine, 0·27	*a*	*Ethyl* 4-*hydroxy*-2-*keto*-6-*morpholinopyran*-3-*carboxylate* (VII)		Plates, EtOH

* (*a*) The base was added slowly with mixing to the chloro-compound in chloroform. The mixture was washed with water, and the chloroform solution evaporated under reduced pressure. (*b*) The mixture obtained as in (*a*) was filtered and the solid washed with water. (*c*) The aqueous base was mixed slowly with a cooled solution of the chloro-compound in dioxan; the mixture was filtered and the filtrate evaporated. (*d*) The reactants, separately dissolved in dry benzene, were mixed and warmed on the steam-bath for several minutes; the mixture was washed with dilute hydrochloric acid, and water, and the benzene solution dried (Na_2SO_4) and evaporated.

† Pet = light petroleum (b. p. 100—120°).

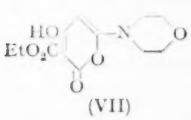
[1] Or (VIII). [2] The crude product was triturated with dry ether. [3] The crude product was triturated with light petroleum (b. p. 80—100°).

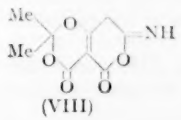
			Found (%)			Required (%)			Light absorption in dioxan	
No.	M. p.	Formula	C	H	N	C	H	N	$\lambda_{max.}$ (Å)	ε
1	182° *	$C_{13}H_{15}O_6N$	55·4	5·4	5·3	55·5	5·4	5·0	2270	17,400
									3360	30,900
2	151·5 *	$C_{14}H_{17}O_5N$	60·0	5·95	5·55	60·2	6·15	5·0	—	—
3	145 *	$C_{13}H_{17}O_5N$	58·4	6·7	5·05	58·4	6·4	5·25	—	—
4	160	$C_{16}H_{15}O_5N$	63·65	5·15	4·9	63·8	5·0	4·65	—	—
5	192·5 *	$C_{15}H_{13}O_5N$	63·1	4·8	4·95	62·7	4·55	4·9	3400	33,000
6	176 *	$C_{16}H_{15}O_5N$	63·9	5·2	5·15	63·8	5·0	4·65	3300	28,300
7	>300 *	$C_9H_9O_5N$	50·9	4·55	6·65	51·2	4·3	6·65	2810	13,000
									3040	13,000 †
8	186 *	$C_{23}H_{19}O_6N$	67·9	4·95	3·4	68·1	4·7	3·5	2270	25,000
									3380	36,500
9	182 *	$C_{24}H_{21}O_5N$	71·55	5·5	3·1	71·45	5·25	3·5	—	—
10	167·5	$C_{23}H_{21}O_3N$	70·65	5·6	3·8	70·55	5·4	3·6	—	—
11	179 *	$C_{25}H_{19}O_5N$	73·2	4·65	3·4	73·4	4·5	3·3	—	—
12	173 *	$C_{23}H_{17}O_5N$	72·5	4·4	3·85	73·0	4·15	3·4	—	—
13	143 *	$C_{15}H_{19}O_6N$	58·15	6·3	4·45	58·2	6·2	4·55	2510	7,700
									2560	7,700
									3330	21,700
14	186 *	$C_{18}H_{17}O_6N$	62·5	5·15	4·1	62·9	5·0	4·1	2270	15,800
									2510	6,200
									2580	6,200
									3370	36,000
15	110·5	$C_{15}H_{19}O_7N$	55·75	5·95	4·65	55·4	5·9	4·3	3330	25,400
16	191 *	$C_{16}H_{19}O_6N$	60·4	6·15	4·1	59·8	5·95	4·35	—	—
17	165	$C_{12}H_{15}O_6N$	54·05	5·85	5·1	53·5	5·6	5·2	2270	14,800
									3250	31,800

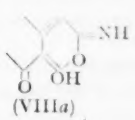
* With decomp. † Similar values in chloroform.

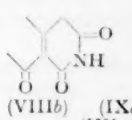
the anilino-compound (III; $R^1 = R^2 = Me$, $R^4 = H$, $R^5 = Ph$) was pseudo-acidic, and with the aqueous hydroxides of lithium, sodium, and potassium (though not with ammonia), it gave sparingly soluble crystalline metal derivatives. Reaction of the sodio-derivative with methyl iodide afforded an *N*-methyl compound. This was identical with (III;

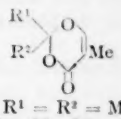
$R^1 = R^2 = R^4 = Me$, $R^5 = Ph$), prepared from the chloropyronodioxin (I; $R^1 = R^2 = Me$) and methylaniline.


(VII)


(VIII)


(VIII*a*)


(VIII*b*)


(IX*a*; $R^1 = R^2 = Me$)
(IX*b*; $R^1 = Me$, $R^2 = Ph$)

With ammonia, the chloropyronodioxin (I; $R^1 = R^2 = Me$) yielded a monosubstitution product as expected, but this had a different absorption spectrum from the previous amine products (III), with less intense maxima at shorter wave-lengths (see Table 1). The ammonia product may therefore exist in the form (VIII) rather than (III; $R^1 = R^2 = Me$, $R^4 = R^5 = H$). The alternative tautomeric form (VIII*a*) could be discounted because the compound lacked enol properties. Moreover the isomeric pyridone structure (VIII*b*) and its tautomeric forms were ruled out because of the ease with which the ring was split, *e.g.*, by morpholine (see below). This lability precluded the condensation of the compound with primary amines in the way possible with other imino-heterocycles (see Elvidge and Linstead, *J.*, 1952, 5000).

4-*Keto*-1 : 3-*dioxins*.—Treatment of the aminopyronodioxins (III) and (VIII) with a further mol. of a primary or secondary amine caused fission of the pyrone ring, and the diamide derivatives (IV) of 4-keto-1 : 3-dioxin were formed (see Table 2). Those derivatives (IV) having $R^4R^5 = R^6R^7$ were also obtained direct from the chloropyronodioxins (I) with the appropriate larger quantity of amine (excess of amine led to acetonetricarboxyamides). The structure of the morpholine product (IV; $R^1 = R^2 = Me$, $NR^4R^5 = NR^6R^7$ = morpholino) was confirmed by degradation with boiling water (or cold sodium hydroxide). Carbon dioxide and acetone were formed, together with enolic acetone-1 : 3-dicarboxymorpholide, the identity of which was verified by a synthesis from diethyl acetone-1 : 3-dicarboxylate and morpholine.

The only previous representatives of the simple 4-keto-1 : 3-dioxins seem to be the parent substance itself (Mejuto and Calvet, *Anal. Fis. Quím.*, 1934, **32**, 1168) and the two derivatives (IX*a* and *b*) (Carroll and Badger, *J. Amer. Chem. Soc.*, 1952, **74**, 6305). Hence the new members (IV) have been examined in some detail. These all absorb light in the 2500—2700-Å region but there are marked substituent effects (see Table 2) as is the case, *e.g.*, with *N*-substituted crotonamides (Crombie, *J.*, 1952, 2997). Qualitative chemical tests showed that the ring was stable to cold water and aqueous hydrochloric acid, and to boiling alcohols and dilute methanolic hydrogen chloride. At pH 9 the Légal and dichlorophenol–indophenol colour tests were negative, and ammoniacal silver nitrate was reduced only when hot. Rupture of the ring occurred with methanolic sodium methoxide, besides boiling water and cold sodium hydroxide, and also with primary and secondary amines.

In containing an enol ether link and an $\alpha\beta$-unsaturated lactone grouping, the 4-keto-1 : 3-dioxin ring system bears an interesting relation to both of the two main types of unsaturated lactone (see Kuehl, Linstead, and Orkin, *J.*, 1950, 2213; also pp. 2223, 2228, and *J.*, 1951, 1501). The properties of the compounds (IV) indicate that they are indeed composite in type. These ketodioxins resemble enol lactones in reacting easily with basic reagents and hot water, but differ from them and resemble $\alpha\beta$-unsaturated lactones in being stable to alcoholic acid and in lacking reducing properties. Carroll and Badger (*loc. cit.*) compared the reactions of ketodioxins with those of diketen.

However, the ease with which the ketodioxin ring reacts under given conditions may perhaps be influenced strongly by the nature of substituents. This is suggested by the differing reactivity of the fused ketopyrano(3′ : 4′-5 : 6)dioxin system to, *e.g.*, alcohols, when substituted by chlorine as in (I) or by amine residues as in (III) : the compounds (I) readily give (II), but the compounds (III) do not react with alcohols alone.

Acetonecarboxylic Acid Derivatives.—The reactions of the easily available chloropyronodioxins (I) and their pyrone (II) and ketodioxin (IV) degradation products with basic reagents provide routes to esters, amides, and mixed ester-amides of acetone-1 : 3-di- and

-1 : 1 : 3-tri-carboxylic acid, which hitherto have been largely inaccessible. The preparations from (I; $R^1 = R^2 = Me$) of triethyl acetone-1 : 1 : 3-tricarboxylate (Part I of this series) and acetone-1 : 3-dicarboxymorpholide (above) were the first examples. The following additional preparations illustrate the scope of the method.

TABLE 2. *Reaction of the aminopyronodioxins* (III) *with* 1 *mol. of various amines :* **4-*keto*-1 : 3-*dioxin*-6-*acetic*-5-*carboxyamides.***

	Aminopyronodioxin (III; $R^1 = R^2 = Me$)			Method,* reaction time	4-Keto-2 : 2-dimethyl-1 : 3-dioxin (IV)		Yield	Form,
No.	NR^4R^5	(g.)	Base (c.c.)	(min.)	NR^4R^5	NR^6R^7	(%)	solvent †
18	Morpholino	0·55	Morpholine, 0·2	*a*, 30	Morpholino	Morpholino	—	EtOAc–Et_2O
19	,,	1·1	$NHEt_2$, 0·45	*a*,[1] 30	Morpholino	NEt_2	52	Prisms, C_6H_6–Pet (b. p. 60—80°)
20	Piperidino	1·4	Morpholine, 0·435	*a*,[2] 25	Piperidino	Morpholino	80	,, ,,
21	NHPh	1	NH_2Ph, 0·32	*b*	NHPh	NHPh	—	Pet (b. p. 100—120°)
22	$NH{\cdot}CH_2Ph$	1	NH_2Bu^n, 0·33	*a*,[3] 40	$NH{\cdot}CH_2Ph$	$NHBu^n$	24	Laths, Pet (b. p. 60—80°)
23	NH_2	0·42	Morpholine, 0·18	*c*	NH_2	Morpholino	50	Needles, EtOH
	Aminopyronodioxin (III; $R^1 = R^2 = Ph$)				2 : 2-Diphenyl-4-keto-1 : 3-dioxin			
	NR^4R^5	(g.)			NR^4R^5	NR^6R^7		
24	Morpholino	1·24	Morpholine, 0·27	*a*, 10	Morpholino	Morpholino	73	EtOH
25	$NHBu^n$	7·1	Morpholine, 1·58	*d*[3]	$NHBu^n$	Morpholino	73	Leaflets, C_6H_6–Pet (b. p. 100—120°)

* (*a*) Heated under reflux in chloroform, and the solution evaporated. (*b*) Heated under reflux in dioxan for 1 hr. The mixture was filtered, the solution evaporated, and the residue triturated with light petroleum (b. p. 40—60°). (*c*) Kept in dioxan at room temperature overnight, and the solution evaporated. (*d*) Shaken in chloroform (50 c.c.) for 1 day at room temp. Unchanged pyronodioxin (1·05 g.) was collected and the filtrate washed with water and evaporated.

† Pet = light petroleum.

[1, 2, 3] The crude product was triturated with (1) light petroleum (b. p. 40—60°), or (2) ether, or (3) light petroleum (b. p. 60—80°).

			Found (%)			Required (%)			Light absorption, (i) in dioxan (ii) in $CHCl_3$	
No.	M. p.	Formula	C	H	N	C	H	N	$\lambda_{max.}$ (Å)	ε
18	134°	$C_{17}H_{24}O_7N_2$	55·8	6·7	7·8	55·4	6·6	7·6	(i) 2270	9,200
									2510	11,100
									2560	11,800
19	117	$C_{17}H_{26}O_6N_2$	57·3	7·3	8·2	57·65	7·4	7·9	—	—
20	131·5	$C_{18}H_{26}O_6N_2$	59·1	7·05	8·05	59·0	7·15	7·65	—	—
21	100	$C_{21}H_{20}O_5N_2$	66·55	5·6	7·25	66·3	5·3	7·35	(ii) 2400	20,900
									2510	17,100
									2900	14,000
22	86	$C_{20}H_{26}O_5N_2$	64·3	7·1	7·45	64·15	7·0	7·5	(ii) 2700	8,600 ‡
									2800	8,600
23	223 (decomp.)	$C_{13}H_{18}O_6N_2$	52·55	6·35	9·45	52·35	6·1	9·4	—	—
24	135	$C_{27}H_{28}O_7N_2$	65·6	6·0	5·6	65·85	5·75	5·7	(i) 2510	11,300
									2570	11,300
									3280	2,200
									3430	2,200
25	117·5	$C_{27}H_{30}O_6N_2$	67·55	6·5	6·35	67·75	6·3	5·85	(ii) 2580	6,900
									2660	7,900
									2760	4,800

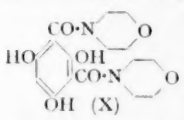
‡ Fluoresced strongly.

The ketodioxin derivative (IV; $R^1 = R^2 = Me$, $R^4 = R^6 = H$, $R^5 = CH_2Ph$, $R^7 = Bu^n$), prepared from (I; $R^1 = R^2 = Me$) by reaction with first benzylamine and then *n*-butylamine, was treated with boiling water. The mixed benzylamide *n*-butylamide (V) of acetone-1 : 3-dicarboxylic acid was thus obtained in good yield. Treatment of the dianilide (IV; $R' = R^2 = Me$) with methanolic sodium methoxide afforded the mixed methyl ester dianilide of acetone-1 : 1 : 3-tricarboxylic acid $NHPh{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Me){\cdot}CO{\cdot}NHPh$. The alternative reaction of aniline with the chloropyrone ester (II; $R^3 = Me$), obtained from

(I; $R^1 = R^2 = Ph$) with methanol, yielded an identical acetonetricarboxylic ester dianilide, so that the structure of this product is certain.

Treatment of the benzylaminopyronodioxin (III; $R^1 = R^2 = Ph$, $R^4 = H$, $R^5 = CH_2Ph$) with 2 mols. of benzylamine afforded enolic acetone-1 : 1 : 3-tricarboxybenzylamide (VI). From each of the chloropyronodioxins (I; $R^1 = R^2 = Me$ and $R^1 = R^2 = Ph$) with an excess of morpholine, enolic acetone-1 : 1 : 3-tricarboxymorpholide (VI) was readily prepared. Its formation from the diphenyl compound (I; $R^1 = R^2 = Ph$) was also carried out stepwise (I) ⟶ (III) ⟶ (IV) ⟶ (VI): benzophenone was a second product at the last stage. The structure of the trimorpholide was confirmed by fission with morpholine at 100°, over 1·4 mols. of malondimorpholide being obtained.

In contrast to the success of the above methods, attempts to synthesise, *e.g.*, acetone-1 : 1 : 3-tricarboxymorpholide by standard routes failed. Triethyl acetone-1 : 1 : 3-tricarboxylate with hot morpholine gave malondimorpholide only. As an alternative it had been hoped to condense malonic half-morpholide acid chloride with a metal derivative of malondimorpholide, but neither the magnesio- nor the sodio-derivative of the latter could be obtained. Dissolution of sodium in molten malondimorpholide caused a self-condensation. We suggest structure (X) for the hygroscopic enolic product, $C_{16}H_{20}O_7N_2$, by analogy with the production of diethyl phloroglucinol-1 : 3-dicarboxylate from malonic ester and sodium (Moore, *J.*, 1904, **85**, 165).



(X)

Experimental

General Properties of Aminopyronodioxins.—The aminopyronodioxins (III) were stable to water and boiling alcohol (no colour with ferric chloride) and did not yield salts with hydrogen chloride in chloroform, or picric acid in dioxan. The 6′-amino(or imino)-compound (No. 7) gave a deep blue-green colour with nitrous acid in aqueous dioxan; this solution afforded no azo-dye with sodium phenoxide. The benzylamino-compound (No. 6) was insoluble in aqueous sodium hydroxide, but the anilino-compound (No. 5) dissolved easily in aqueous lithium, sodium, potassium, and ammonium hydroxide; crystalline metal derivatives separated rapidly from the first three solutions.

Methylation of 6′-Anilino-2′ : 4-diketo-2 : 2-dimethylpyrano(3′ : 4′-5 : 6)-1 : 3-dioxin.—When stirred with sodium hydroxide (0·245 g., 2 mols.) in water (10 c.c.) the anilino-compound (No. 5) (0·88 g.) dissolved, and after a few minutes the sodio-derivative (0·95 g.) separated as needles. A portion (0·53 g.) in methanol was kept with excess of methyl iodide overnight. The solution was evaporated and the residue triturated with water to remove sodium iodide. From ethanol, the product (0·34 g., 66%) formed needles, m. p. 160° alone and when mixed with 2′ : 4-diketo-2 : 2-dimethyl-6′-methylanilinopyrano(3′ : 4′-5 : 6)-1 : 3-dioxin (No. 4).

General Properties of the 4-Keto-1 : 3-dioxin Derivatives (IV).—None of the compounds (IV) gave a colour with ferric chloride in aqueous dioxan. The dimorpholide (No. 18) and the morpholide amide (No. 23) were easily water-soluble. Their stability to various reagents was investigated by testing for enolic products with ferric chloride, after any excess of acid or alkaline reagent had first been neutralised. With dioxin No. 18 in the cold the test was negative after treatment with aqueous hydrochloric acid for 1 hr. or (also with Nos. 19 and 20) with water for 3 days, and under reflux with methanolic hydrogen chloride (1 hr.), methanol (10 min.), or butanol (5 min.); with boiling aqueous sodium hydroxide or methanolic sodium methoxide there was a purple and a deep red colour respectively after 5 min.; with boiling water, Nos. 18, 19, and 20 gave a purple colour in the test after 10 min.

Tests for reducing properties were performed on dioxin No. 20, by methods described by Kuehl, Linstead, and Orkin (loc. cit.) (see p. 2253).

Reaction of the Chloropyronodioxin (I; $R^1 = R^2 = Me$) *with 3 Mols. of Morpholine.*—Solutions of the chloro-compound (1 g.) in benzene (40 c.c.), and of morpholine (2·5 c.c.) in benzene (10 c.c.), were heated together under reflux for 5 min. The mixture was washed with dilute hydrochloric acid and water, the benzene layer was combined with three chloroform extracts of the aqueous washings, dried (Na_2SO_4), and evaporated, and the residue triturated with dry ether. The product (1·3 g., 81%) crystallised from ethyl acetate–ether and had m. p. 134° alone and in admixture with the dimorpholide of 4-keto-2 : 2-dimethyl-1 : 3-dioxin-6-acetic-5-carboxylic acid (No. 18).

Degradation of the Dimorpholide of 4-Keto-2 : 2-dimethyl-1 : 3-dioxin-6-acetic-5-carboxylic

Acid.—The preceding dioxin derivative (No. **18**) (0·5 g.) was heated with water under reflux for 2 hr., during which carbon dioxide was evolved. The solution was distilled almost to dryness; the distillate with Brady's reagent gave acetone **2** : **4**-dinitrophenylhydrazone, m. p. and mixed m. p. 125°. The residue in the distillation flask was dried under reduced pressure, then triturated with ether, affording acetone-**1** : **3**-dicarboxymorpholide (0·3 g., 78%), m. p. 132° undepressed by the authentic material described below.

Acetone-**1** : **3**-*dicarboxymorpholide.*—(*a*) Diethyl acetone-**1** : **3**-dicarboxylate (**10** g.) was heated with morpholine (**10·25** c.c.) at 75° for **19** hr., and the product (5·2 g., 37%) precipitated by addition of benzene. From ethanol, *acetone*-**1** : **3**-*dicarboxymorpholide* formed needles, m. p. 132° (Found: C, 54·85; H, 7·05; N, 10·0. $C_{13}H_{20}O_5N_2$ requires C, 54·9; H, 7·1; N, 9·85%). It gave a purple colour with aqueous ferric chloride. The m. p. was depressed to 110° by malondimorpholide.

(*b*) The foregoing dioxin-dimorpholide (No. **18**) (1·1 g.) in water (10 c.c.) was heated with 2N-sodium hydroxide (1·5 c.c.) at 100° for 10 min. The cooled solution was neutralised with aqueous sulphuric acid (evolution of carbon dioxide), and extracted with chloroform (3 × 10 c.c.), evaporation of which gave acetone-**1** : **3**-dicarboxymorpholide (0·58 g., 68%), m. p. and mixed m. p. 131°.

Acetone-**1**-*carboxybenzylamide*-**3**-*carboxy*-n-*butylamide.*—6′-Benzylamino-2′ : 4-diketo-**2** : 2-dimethylpyrano(3′ : 4′-5 : 6)-**1** : **3**-dioxin (No. **6**) (**1** g.) was heated with *n*-butylamine (**0·33** c.c.) in chloroform (10 c.c.) under reflux for 1 hr. Evaporation of the chloroform afforded the crude oily ketodioxin derivative, which was boiled with water for 2·5 hr. From water, *acetone*-**1**-*carboxybenzylamide*-**3**-*carboxy*-n-*butylamide* (0·3 g., 31%) crystallised with m. p. 139° (Found: C, 65·9; H, 7·85; N, 9·55. $C_{16}H_{22}O_3N_2$ requires C, 66·2; H, 7·65; N, 9·65%).

1-*Carbomethoxyacetone*-**1** : **3**-*dicarboxyanilide.*—(*a*) 4-Keto-**2** : 2-dimethyl-**1** : **3**-dioxin-**6**-acetanilide-**5**-carboxyanilide (No. **21**) (**150** mg.) in methanol was heated under reflux for 15 min. with sodium methoxide (from 9 mg. of sodium). The cooled solution was poured into aqueous hydrochloric acid, whereupon the acetonetricarboxylic ester dianilide (**100** mg., 71%) separated, m. p. 214° (decomp.) undepressed by the specimen obtained in the following experiment.

(*b*) Methyl 6-chloro-4-hydroxy-2-ketopyran-3-carboxylate (Part I, *loc. cit.*) (0·5 g.) in chloroform was warmed with aniline (**0·45** c.c.) for several minutes. The mixture was shaken with water, and the chloroform separated and evaporated. *Carbomethoxyacetone*-**1** : **3**-*dicarboxyanilide* (**0·53** g., 64%) crystallised from benzene and had m. p. 213° (decomp.) (Found: C, **64·25**; H, **4·95**; N, **7·6**. $C_{19}H_{18}O_5N_2$ requires C, 64·4; H, 5·1; N, 7·9%). It gave a deep red colour with ferric chloride in aqueous dioxan.

Acetone-**1** : **1** : **3**-*tricarboxybenzylamide.*—6′-Benzylamino-2′ : 4-diketo-**2** : 2-diphenylpyrano-(3′ : 4′-5 : 6)-**1** : **3**-dioxin (No. **11**) (**0·5** g.) and benzylamine (**0·26** c.c., 2 mols.) in dimethylformamide (7 c.c.) were kept for **15·5** hr. Evaporation of the solution under reduced pressure, and trituration of the residue with light petroleum (b. p. 60—80°) yielded *acetone*-**1** : **1** : **3**-*tricarboxybenzylamide* (**0·44** g., 81%) which crystallised from benzene–light petroleum (b. p. 60—80°) and had m. p. **100°** (Found: N, **9·55**. $C_{27}H_{27}O_4N_3$ requires N, 9·2%). It gave a deep red colour with alcoholic ferric chloride.

Acetone-**1** : **1** : **3**-*tricarboxymorpholide.*—(*a*) **6′**-Chloro-**2′** : 4-diketo-**2** : 2-dimethylpyrano(**3′** : 4′-5 : **6**)-**1** : **3**-dioxin (Part I) (**0·41** g.) in chloroform was gradually treated with morpholine (**0·31** c.c., 2 mols.). The solution was shaken with water, and the chloroform layer was dried (Na_2SO_4) and kept with morpholine (**0·31** c.c.) overnight. Evaporation yielded *acetone*-**1** : **1** : **3**-*tricarboxymorpholide* which crystallised from ethanol as needles, m. p. 181° (Found: C, 54·9; H, 7·0; N, 10·4. $C_{18}H_{27}O_7N_3$ requires C, 54·4; H, 6·85; N, 10·55%). It gave a red-purple colour with aqueous ferric chloride.

(*b*) The tricarboxymorpholide was also obtained by keeping the chloro-**2** : 2-diphenylpyronodioxin (I; $R^1 = R^2 =$ Ph) with an excess of morpholine in chloroform.

(*c*) 4-Keto-**2** : 2-diphenyl-**1** : **3**-dioxin-**6**-acetomorpholide-**5**-carboxymorpholide (No. **24**) (0·5 g.) was heated with morpholine (**0·09** c.c.) in dioxan on the steam-bath for **15** min. The solution was evaporated, and the residue washed with ether, yielding acetone-**1** : **1** : **3**-tricarboxymorpholide (**0·4** g.) with m. p. and mixed m. p. **181°** after recrystallisation from ethanol. The ethereal washings contained benzophenone which was isolated as the **2** : 4-dinitrophenylhydrazone, m. p. and mixed m. p. **232°**.

Fission to Malondimorpholide.—The tricarboxymorpholide (**0·23** g.) was heated with morpholine (**0·51** c.c., 10 mols.) on the steam-bath for **15** hr. Trituration with ether yielded malondimorpholide (**0·2** g., **1·4** mols.), m. p. **132°** undepressed by authentic material.

The latter was obtained in good yield by heating diethyl malonate (100 g.) with an excess of morpholine (135 g.) at 150° for 42 hr. *Malondimorpholide* crystallised from ethanol as plates, m. p. 137° (Found: C, 54·25; H, 7·45; N, 11·25. $C_{11}H_{18}O_4N_2$ requires C, 54·5; H, 7·5; N, 11·6%).

Action of Morpholine on Triethyl Acetone-1 : 1 : 3-tricarboxylate.—The triester (5·5 g.) was heated with morpholine (5·2 c.c.) at 75° for 22 hr. The product gave no colour with aqueous ferric chloride. Treatment with benzene yielded malondimorpholide (2·75 g.), m. p. 135° undepressed by authentic material.

Malonic Monoethyl Ester Morpholide.—Diethyl malonate (160 g.) and morpholine (87 g., 1 mol.) were heated at 150° for 24 hr. Malondimorpholide (41 g.) was filtered off and washed with ether, and the filtrate was distilled under reduced pressure, yielding *malonic monoethyl ester morpholide* (84 g., 42%), b. p. 135—145°/1·5 mm., m. p. 59·5° [from light petroleum (b. p. 40—60°)] (Found: C, 53·55; H, 7·6; N, 6·45. $C_9H_{15}O_4N$ requires C, 53·7; H, 7·5; N, 6·95%).

Attempted Preparation of Metal Derivatives of Malondimorpholide.—The morpholide was treated with magnesium methoxide (1 mol.) in methanol and the solution evaporated to dryness. The residue was suspended in dry benzene and acetyl chloride added. Heat was evolved. Evaporation, treatment with aqueous acid, and extraction with chloroform gave malondimorpholide (recovery, 75%).

Repetition of the reaction, with sodium and formamide–dioxan, instead of magnesium methoxide in methanol, yielded only malondimorpholide.

Action of Sodium on Molten Malondimorpholide.—Malondimorpholide (4·84 g.) was heated with sodium (0·23 g.) until the metal had dissolved. Morpholine vapour was evolved. After being cooled, the product was treated with water (20 c.c.), and the solution was washed with chloroform (5 × 10 c.c.), acidified, clarified, and extracted with chloroform (5 × 25 c.c.). Evaporation of the latter and trituration of the residue with ether afforded *phloroglucinol-dicarboxymorpholide* which separated from dioxan–ether as a pale yellow powder, m. p. 227° (Found: C, 55·2; H, 5·75; N, 8·05. $C_{16}H_{20}O_7N_2$ requires C, 54·55; H, 5·7; N, 7·95%). It gave a deep red colour with aqueous ferric chloride.

Analyses were performed in the micro-analytical laboratory (Mr. F. H. Oliver), and light-absorption measurements in the spectrographic laboratory (Mrs. A. I. Boston) of this Department. We thank Professor R. P. Linstead, C.B.E., F.R.S., for his kind interest, and the Department of Scientific and Industrial Research for a maintenance grant (to S. J. D.).

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465. *Studies on Phosphorylation. Part XI.* The Reaction between Carbodi-imides and Acid Esters of Phosphoric Acid. A New Method for the Preparation of Pyrophosphates.*

By H. G. Khorana and A. R. Todd.

Di-*p*-tolyl- and di*cyclo*hexyl-carbodi-imides react with mono- and di-esters of phosphoric acid at room temperature to yield the corresponding symmetrical di- and tetra-esters of pyrophosphoric acid. Reaction is almost instantaneous and the yields well-nigh quantitative.

In Part X * of this series, methods for the preparation of tetra-esters of pyrophosphoric acid were discussed, and their production from diesters of phosphoric acid by means of exchange reactions was described. An important feature of this new method was that it did not involve the use of phosphorochloridates (chlorophosphonates), which are sometimes difficultly accessible in the nucleotide field (cf. Mason and Todd, Part VIII, *J.*, 1951, 2267). Since it was desirable to have available as wide a range of methods for polyphosphate preparation as possible, in view of our researches directed towards the synthesis of nucleotide coenzymes, further investigations were undertaken.

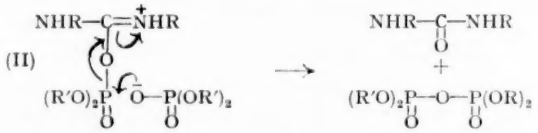
* Part X, *J.*, 1952, 1234.

The reactions of carbodi-imides with carboxylic acids have been extensively studied by Zetzsche and his collaborators (*Ber.*, 1938, **71**, 1088, and subsequent papers). In general two reactions were observed, (*a*) the formation of *N*-acylureas and (*b*) the formation of acid anhydrides and ureas :

$$(R'\cdot CO)_2O + CO(NHR)_2 \xleftarrow{b} R\cdot N{:}C{:}N\cdot R + R'\cdot CO_2H \xrightarrow{a} R'\cdot CO\cdot NR\cdot CO\cdot NHR$$
(I)

As a rule, aromatic carbodi-imides reacted by route (*a*), whereas aliphatic carbodi-imides gave mainly the anhydrides [reaction (*b*)] or mixtures of the products expected from reactions (*a*) and (*b*). As far as we are aware the reaction of carbodi-imides with acids other than carboxylic acids, and hydrochloric and hydrocyanic acids, has not been studied, but it might be expected that, particularly if dialkyl carbodi-imides were used, anhydride formation would occur. Dibenzyl hydrogen phosphate was therefore treated with di-*cyclo*hexylcarbodi-imide (I; $R = C_6H_{11}$) at room temperature in a variety of inert solvents. In every case separation of *NN'*-di*cyclo*hexylurea was almost instantaneous, and from the solution tetrabenzyl pyrophosphate was isolated in excellent yield. Similar results were obtained with di-*p*-tolylcarbodi-imide. The reaction appears to be general, since tetraphenyl pyrophosphate and tetra-*p*-nitrophenyl pyrophosphate could be prepared similarly. When di*cyclo*hexylcarbodi-imide was used there was some difficulty in isolating tetra-*p*-nitrophenyl pyrophosphate owing to the similar solubility of the substituted urea, but its formation was demonstrated by reaction with *cyclo*hexylamine. By using di-*p*-tolylcarbodi-imide in dioxan this difficulty was overcome : the sparingly soluble *NN'*-di-*p*-tolylurea separated and from the residual solution tetra-*p*-nitrophenyl pyrophosphate was readily isolated.

A detailed discussion of the mechanism of the reactions of carbodi-imides with acids of various types is reserved until further studies can be reported, but it may be observed that the first step in pyrophosphate production is almost certainly the formation of a cation of type (II), which is further attacked by a second phosphate anion to yield the urea and pyrophosphate. The rate of formation of the intermediate (II) will be a function of the strength of the acid employed, and the observed well-nigh instantaneous formation of pyrophosphate from diesters of phosphoric acid is in accord with this mechanism. This contrasts with the factors governing the production of pyrophosphates by the exchange reactions discussed in Part X (*loc. cit.*) : in them the anhydride of a diester of phosphoric acid is always converted into a less reactive anhydride. Thus the very reactive tetra-*p*-nitrophenyl pyrophosphate, which is readily prepared by the carbodi-imide method, could not be prepared by exchange reactions using triethylammonium di-*p*-nitrophenyl phosphate and either tetraphenyl pyrophosphate or trifluoroacetic anhydride (Part X; *loc. cit.*).



It also follows that in the attack on the intermediate (II) leading to pyrophosphate formation, the anions of the acid used would be much more effective than neutral water molecules, *i.e.*, that it should be possible to observe formation of the anhydride even in presence of moderate amounts of water. Zetzsche and his colleagues (*locc. cit.*), indeed, observed that reactions involving carbodi-imides were largely unaffected by traces of water. Since, in the nucleotide field, where we hope to use this method of pyrophosphate preparation, it would frequently be advantageous (on solubility grounds) to carry out the reaction in media containing water, a series of experiments has been carried out in which the reaction between dibenzyl hydrogen phosphate (2 mols.) and di*cyclo*hexylcarbodi-imide (1 mol.) was studied in methyl cyanide containing various amounts of water. Although the yield of tetrabenzyl pyrophosphate decreased with increasing water content (see

Experimental), it is worthy of note that even when a large excess (100 mols.) of water was present the yield was still of the order 50%. It thus appears that essentially complete formation of pyrophosphate could be attained in presence of moderate amounts of water provided a substantial excess of the carbodi-imide were used.

Many of the nucleotide coenzymes (*e.g.*, cozymase) are di-esters of pyrophosphoric acid and, although their synthesis might well be effected by first preparing a tetra-ester and subsequently removing two of the unwanted ester groups, it was clearly of interest to see whether the carbodi-imide method would offer a direct route to the production of diesters. Accordingly phenyl dihydrogen phosphate was brought into reaction with di*cyclo*hexylcarbodi-imide in the usual way; *s*-diphenyl dihydrogen pyrophosphate, PhO·PO(OH)·O·PO(OH)·OPh, was isolated in good yield and characterised as its bis-*cyclo*hexylammonium salt.

Experimental

Tetrabenzyl Pyrophosphate.—Di*cyclo*hexylcarbodi-imide (227 mg., 1·1 mols; Schmidt, Hitzler, and Lahde, *Ber.*, 1938, **71**, 1933) in dry ether (1 c.c.) was added to dibenzyl hydrogen phosphate (556 mg., 2 mols.) in dry ether (5 c.c.). *NN'*-Di*cyclo*hexylurea began to separate almost at once, and after 30 min. was filtered off. The colourless filtrate was evaporated and the residue recrystallised from chloroform–light petroleum (b. p. 40—60°), giving tetrabenzyl pyrophosphate (90%), m. p. 61—62° alone or mixed with an authentic sample (m. p. 61—62°).

The same reaction was also carried out with benzene or methyl cyanide in place of ether, the yields being 87% and 82% respectively. Dimethylformamide was less convenient since separation of the urea was incomplete until the solution was evaporated and stirred with ether. With ether as solvent and di*cyclo*hexylcarbodi-imide replaced by di-*p*-tolylcarbodi-imide (Zetzsche and Nerger, *Ber.*, 1940, **73**, 467), the yield of tetrabenzyl pyrophosphate was 93%.

Effect of Tertiary Bases on Formation of Tetrabenzyl Pyrophosphate.—To a solution of dibenzyl hydrogen phosphate (556 mg., 2 mols.) in benzene (3 c.c.) pyridine (0·16 c.c., *ca.* 2 mols.) was added, followed by di*cyclo*hexylcarbodi-imide (227 mg., 1·1 mols.). Di*cyclo*hexylurea was filtered off after 15 min. and the filtrate evaporated. The residual oil solidified when shaken with ice-water, yielding directly practically pure tetrabenzyl pyrophosphate (93%).

When triethylamine was used in place of pyridine no di*cyclo*hexylurea separated.

Effect of Water on the Formation of Tetrabenzyl Pyrophosphate.—Di*cyclo*hexylcarbodi-imide (120 mg.) in dry methyl cyanide (10 c.c.) was mixed rapidly with a solution of dibenzyl hydrogen phosphate (278 mg.) in methyl cyanide (10 c.c.), to which had been added various amounts of water; an apparatus similar to that described by Grewe and Nolte (*Annalen*, 1951, **575**, 11) was used. The amount of unchanged acid was estimated immediately by dilution with water and titration with alkali (phenolphthalein). The results are given in the following table (10·46 c.c. of alkali were equivalent to 278 mg. of dibenzyl hydrogen phosphate) :

Water added (c.c.)	Nil	1	2	4
Alkali used (c.c.)	0·94	5·34	7·68	9·6
Yield of tetrabenzyl pyrophosphate (%) ...	91	49	26·6	8·3

Tetraphenyl Pyrophosphate.—When ethereal di*cyclo*hexylcarbodi-imide (230 mg., 1·1 mols.) was added to anhydrous diphenyl hydrogen phosphate (500 mg., 2 mols.) in ether, quantitative separation of di*cyclo*hexylurea occurred almost at once. Filtration, followed by evaporation of the filtrate, gave tetraphenyl pyrophosphate as a viscous oil; the product was assayed by reaction with excess of *cyclo*hexylamine (Corby, Kenner, and Todd, Part X), giving diphenyl *N*-*cyclo*hexylphosphoramidate (92%) and *cyclo*hexylammonium diphenyl phosphate (96%).

Tetra-p-nitrophenyl Pyrophosphate.—Ether could not be employed as solvent owing to the very low solubility of di-*p*-nitrophenyl hydrogen phosphate and, although somewhat better, nitromethane, acetonitrile, and chloroform did not give satisfactory results. In preliminary experiments with di*cyclo*hexylcarbodi-imide and dioxan, however, it was clear that the desired pyrophosphate was formed, since treatment of the reaction mixture with *cyclo*hexylamine yielded di-*p*-nitrophenyl *N*-*cyclo*hexylphosphoramidate; the following method was finally adopted.

Di-*p*-nitrophenyl hydrogen phosphate (2·33 g.) was dissolved in a minimum of warm anhydrous dioxan (*ca.* 15 c.c.). The solution was rapidly cooled, and di-*p*-tolylcarbodi-imide (1·54 g.) added. *NN'*-Di-*p*-tolylurea (700 mg.) separated at once, and was removed by rapid filtration. The filtrate was now evaporated *in vacuo*, giving an oil which was dissolved in a

small amount of dry benzene. Gradual addition of light petroleum (b. p. 40—60°) at intervals during 24 hr. completed crystallisation of the crude product, which was dissolved in warm dioxan (7—8 c.c.). After filtration from a small amount of *NN'*-di-*p*-tolylurea the solution was set aside. The *tetra*-p-*nitrophenyl pyrophosphate* which separated (1·2 g.) was recrystallised from dioxan, forming stout, almost colourless prisms. Heated in a vacuum the pure substance, which is very susceptible to moisture, melted at 126—127°, then re-solidified and melted at 146—148° (Found: C, 44·0; H, 2·8; N, 8·3. $C_{24}H_{16}O_{15}N_4P_2$ requires C, 43·6; H, 2·4; N, 8·5%).

Treated with *cyclo*hexylamine in warm methyl cyanide the product yielded di-*p*-nitrophenyl *N-cyclo*hexylphosphoramidate (93%; m. p. and mixed m. p. 174—176°) and *cyclo*hexylammonium di-*p*-nitrophenyl phosphate (91%).

s-*Diphenyl Dihydrogen Pyrophosphate*.—Ethereal solutions of phenyl dihydrogen phosphate (174 mg., 1 mol.) and di*cyclo*hexylcarbodi-imide (226 mg., 1·1 mols.) were rapidly mixed, with shaking. The oil which separated almost immediately was converted into a crystalline powder by prolonged trituration, and was then collected and washed with ether. The powder was extracted successively with portions (2—3 c.c.) of cold water until the extracts were no longer acidic. To the combined extracts (*ca.* 10 c.c.), aqueous *cyclo*hexylamine was added to pH 8, and the solution set aside at 0°. s-*Bis*cyclo*hexylammonium diphenyl pyrophosphate* which separated crystallised from water as colourless needles, m. p. 250—255° (62—76%) (Found: C, 55·0; H, 7·3; N, 5·4. $C_{24}H_{38}O_7N_2P_2$ requires C, 54·6; H, 7·3; N, 5·3%). Electrometric titration of the salt with acid and alkali showed the absence of secondary phosphoryl dissociation in the pH range 4·5—8·5; the back-titration curve from pH 10, however, showed a kink at pH *ca.* 7·5, presumably due to a small amount of hydrolysis.

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466. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part I.* AH_2 *Molecules.*

By A. D. WALSH.

The electronic orbitals possible for an AH_2 molecule when linear are correlated with those possible for the molecule when non-linear. Qualitative curves of binding energy *versus* ∠HAH are given for the various orbitals. These curves are then used to explain and predict (i) the shapes and (ii) the electronic spectra and associated characteristics of AH_2 molecules. AH_2 molecules containing 4 valency electrons should be linear in their ground states. AH_2 molecules containing 5—8 valency electrons should be bent in their ground states.

THE purpose of this paper is first to correlate the electronic orbitals of a bent with a linear AH_2 molecule, next to decide whether a given orbital becomes more or less tightly bound with increase of the angle HAH, and then to use the resulting graphs of binding energy *versus* apex angle to explain and predict the shapes and spectra of AH_2 molecules.

Linear AH_2 *Molecules*.—The lowest-energy intra-valency-shell orbitals of a linear AH_2 molecule, may, on the assumption that these are built solely from *s* and *p* atomic orbitals, be described as follows: (i) Two orbitals binding the hydrogen atoms to the central atom. These may be thought of as each formed by the overlap of an *sp* hybrid atomic orbital on *A* with the 1*s* orbital of hydrogen. If so regarded they will be orbitals of σ-type predominantly localized one in each A–H distance. If, however, one were discussing a transition involving excitation of an electron from one of the bonding orbitals, one could not regard the electron as coming from one A–H link or the other—the two are indistinguishable. If one first conceives of the orbitals as completely localized one has to take combinations of them in order to express this indistinguishability. These combinations are either in-phase or out-of-phase and may be labelled σ_g and σ_u respectively. (ii) A π_u orbital. This is simply a *p* orbital localized on the central atom and pointing in a direction at 90° to the HAH line. It is non-bonding. Since there are two such directions that are independent but equivalent (except for a rotation by 90°), the orbital is two-fold

degenerate. If the apex angle were changed from 180°, the degeneracy must become split. The order of decreasing binding energy of these orbitals is σ_g, σ_u, π_u.

Bent AH_2 *Molecules.*—A bent AH_2 molecule belongs to the symmetry class C_{2v}. The definitions of the symbols appropriate to the non-localized orbitals of such a molecule are given below. The z axis bisects the HAH angle and lies in the molecular plane. The y axis also lies in the molecular plane and is parallel with the H ··· H line. $C_2(z)$ means a rotation by 180° about the z axis. $\sigma_v(y)$ means a reflection in the xz plane. + and − mean respectively that the wave function does not or does change sign when one of the symmetry operations $C_2(z)$ or $\sigma_v(y)$ is carried out.

	$C_2(z)$	$\sigma_v(y)$
a_1	+	+
a_2	+	−
b_1 *	−	+
b_2 *	−	−

* Certain authors reverse the definitions of b_1 and b_2.

The lowest-energy intra-valency-shell orbitals of an AH_2 molecule whose apex angle is 90° are then as follows: (i) Two orbitals binding the hydrogen atoms to the central atom. These may be thought of, in the first place, as each formed by the overlap of a pure p atomic orbital on A with the 1s orbital of H. This would be to think of the orbitals as predominantly localized, one in each A–H distance. As with the bonding orbitals of the linear molecule, however, for discussions of spectroscopic transitions involving these orbitals they must be regarded as non-localized. The equivalent non-localized orbitals are simply the in-phase or out-of-phase combinations of the two localized orbitals, and, being no longer localized, may, by the above table of definitions, be labelled a_1 and b_2 respectively. (ii) A p orbital on atom A pointing in the x direction. The foregoing Table shows that the molecular symbol to be applied to this orbital is b_1. (iii) An s orbital on atom A. It is non-bonding. The Table shows that the molecular symbol to be applied to this orbital is a_1.

Correlation of the Orbitals for Bent and Linear Molecules.—Clearly, if the HAH angle is gradually increased, the a_1 and the b_2 bonding orbitals must eventually become the σ_g and the σ_u orbitals respectively of the linear molecule. At the same time the binding energy of the orbitals must increase. The reasons for this may be seen by thinking of the orbitals in either their localized or their non-localized forms. For the localized forms, the reasons are: (1) the orbitals are built solely from p atomic orbitals of A in the 90° molecule but partly from an s atomic orbital of A in the linear molecule; (2) an sp hybrid valency gives rise to a stronger bond than does a pure p valency (see Walsh, *Discuss. Faraday Soc.*, 1947, **2**, 18).

When considering the non-localized forms, it is convenient to form first the two possible group orbitals of the H_2 group, *viz.*, 1s + 1s and 1s − 1s. To do this automatically takes account of the symmetry of the molecule. The components from which the non-localized molecular orbitals are built may then be written as follows:

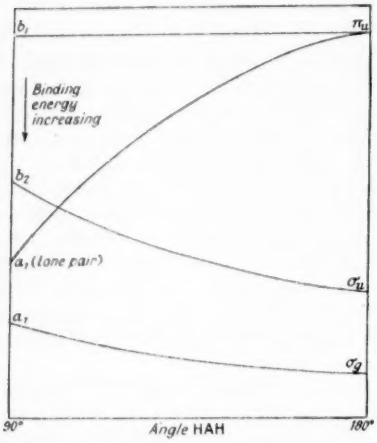
Bent molecule		Linear molecule	
1s + 1s, a_1	p_z, a_1	1s + 1s, σ_g	$p_z p_z$, π_u
1s − 1s, b_2	p_y, b_2	1s − 1s, σ_u	p_y, σ_u
s_A, a_1	p_x, b_1	s_A, σ_g	

Components of the same species may then be "mixed" to form the actual molecular orbitals. This procedure leads to the same end as taking combinations of the localized orbitals. We now introduce three principles: (i) in the 90° molecule the s_A orbital does not mix ("hybridize") with the other orbitals *; (ii) whether or not an orbital becomes more tightly bound with change of angle is determined primarily by whether or not it changes from being built from a p orbital of A to being built from an s orbital of A; and (iii) if no change of A valencies from which the orbital is built occurs when the angle is changed, the following subsidiary effect determines whether the orbital becomes more

* Introduced to make the description of the non-localized bond orbitals consistent with that of the localized ones.

or less tightly bound: if the orbital is anti-bonding between the end atoms it is most tightly bound when the latter are as far apart as possible (*i.e.*, in the linear molecule); if it is bonding between the end atoms it is most tightly bound when the latter are as near together as possible (*i.e.*, in the 90° molecule). The a_1–σ_g bond orbital is thus built from a combination of 1*s* + 1*s* and p_z in the 90° molecule, from a combination of 1*s* + 1*s* and s_A in the linear molecule, and from a combination of 1*s* + 1*s*, s_A, and p_z in the intermediate molecule. It follows that the orbital is more tightly bound in the linear than in the bent molecule. The b_2–σ_u orbital is built from a combination of the 1*s* — 1*s* and p_y components in both the bent and the linear molecule; but from principle (iii), it is more tightly bound in the linear molecule since it is anti-bonding between the end atoms.

Clearly, as the HAH angle is increased, the b_1 orbital of the bent molecule must become one of the two π_u orbitals of the linear molecule. To a first approximation, the orbital is the same when the apex angle is 90° as when it is 180°. We may therefore suppose its binding energy to remain approximately constant as the angle changes.



Increase of the apex angle from 90° implies mixing of the a_1s_A orbital with the a_1p_z orbital on A. The a_1 bond orbital, instead of being built from a pure *p* valency of A, becomes more and more built also from the *s* orbital of A; while at the same time the non-bonding orbital, instead of being built solely from the pure *s* orbital of A, becomes more and more built from a p_z orbital on A. In the linear molecule, the bonding orbital has become built from an orbital of A that is solely *s*, while the non-bonding orbital has become built solely from a p_z orbital of A. In other words, as the HAH angle increases from 90° to 180°, the bond orbital increases in binding energy, while the non-bonding orbital originally labelled a_1s_A decreases in binding energy until at 180° it becomes one of the degenerate π_u orbitals.

At 90° the non-bonding a_1s_A orbital must be much more tightly bound than the non-bonding b_1p orbital. Where it lies in relation to the b_2 and a_1 bond orbitals is best decided by appeal to experimental facts.

Shapes of Actual AH_2 *Molecules.*—The Figure is a correlation diagram between the orbitals possible for bent and linear AH_2 molecules. It incorporates the conclusions reached above as to whether a particular orbital rises or falls in energy as the HAH angle is changed.*

The Figure does not include *all* the possible intra-valency-shell orbitals, but only the lowest-lying ones. Two others are possible and are referred to below. There is no particular reason to make the Figure include all and only all the intra-valency-shell orbitals; for an infinite number of extra-valency-shell orbitals is also possible, the lowest of which (see the discussion below of the spectrum of water vapour) will be comparable in energy with the highest intra-valency-shell orbitals. It is just as arbitrary to make the Figure show six orbitals as to make it show four; and, indeed, for the purpose of interpreting observed spectra it is less desirable since it is the highest intra-valency-shell orbitals that are most likely to lie above or mix with the lowest extra-valency-shell orbitals. There is no doubt about the four lowest-lying orbitals—they are intra-valency-shell in type; but the fifth and sixth orbitals in order of energy are probably not both simple intra-valency-shell orbitals. A similar point should be borne in mind in reading all the

* *Added in Proof.*—The drop from left to right of the a_1–σ_g orbital curve, due to principle (ii), is offset by a smaller rise due to principle (iii). The rise from left to right of the a_1–π_u orbital curve is not offset. The Figure has therefore been drawn with the a_1–σ_g and b_2–σ_u curves falling from left to right by similar amounts; and both falling considerably less than the a_1–π_u curve rises.

papers of this series, where the correlation diagrams show what are thought to be the lowest energy orbitals and do not necessarily include *all* the intra-valency shell orbitals.

Each of the curves must be a maximum or a minimum on the 180° line, since from 180° to 270° the curves must repeat their behaviour from 180° to 90°. The two most tightly bound orbitals have a minimum on the 180° line. One therefore expects that all AH_2 molecules containing only four valency electrons will be linear in their ground states. As far as is known, this is true. As examples, the BeH_2 and HgH_2 molecules are expected to be linear in their ground states. On the other hand, the ground states of AH_2 molecules containing 5, 6, 7, or 8 valency electrons are expected to be bent because at least one electron has to be placed in the a_1 non-bonding orbital. Similarly, the first excited state of HgH_2 or BeH_2 should be bent. This a_1 orbital rises steeply from left to right in the Figure because, as already explained, it changes from a pure *s* orbital to a pure *p* orbital. The ground state of the H_2O molecule, with eight valency electrons, has therefore a bent nuclear configuration. The CH_2 molecule, with six valency electrons, is similarly expected to be bent. The actual value of the apex angle cannot be predicted, while the Figure remains merely qualitative. If the angle is close to 180°, the ground state of the molecule may be a triplet, the configuration

$$(a_1)^2(b_2)^2(a_1)(b_1),{}^3B_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

lying lower in energy than

$$(a_1)^2(b_2)^2(a_1)^2,{}^1A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

because the existence of electron repulsion offsets the small energy difference of the (a_1) and (b_1) orbitals. If, on the other hand, the apex angle is considerably less than 180°, the ground state will be a singlet, having the configuration (2). By analogy with H_2O and in view of the fact that the two most weakly bound electrons of the H_2O molecule lie in the b_1 orbital and should therefore have comparatively little effect on the apex angle, the second possibility seems the more likely.

The small decrease that has been observed in the apex angle in the series H_2O, H_2S, H_2Se, H_2Te may be due either to the a_1–π_u curve rising even more steeply or to the bonding orbital curves falling less steeply as one passes from H_2O to H_2Te. However, the total range of the decrease is only 14°.

Spectra of AH_2 *Molecules.*—(i) *Spectrum of* H_2O. In the ground state of the H_2O molecule all the orbitals represented in the Figure are fully occupied. These are the only low-lying orbitals of the molecule. No electronic spectrum of H_2O is therefore expected until comparatively short wave-lengths are reached. In agreement, the first absorption of the molecule occurs as a continuum between 1830 and 1500 Å ($\lambda_{max.}$ *ca.* 1675 Å; Hopfield, *Phys. Review*, 1950, **77**, 560).

In the Figure the b_2 and the upper a_1 curve have been drawn to cross at an angle of *ca.* 110°. The reason for this is as follows. Three ionization potentials of H_2O are known (Price and Sugden, *Trans. Faraday Soc.*, 1948, **44**, 108, 116), *viz.*, 12·61 v, 14·5 ± 0·3 v, 16·2 ± 0·3 v. A good Rydberg series is known leading to the first limit (Price, *J. Chem. Phys.*, 1936, **4**, 147). A cruder Rydberg series is also known leading to the third limit (Henning, *Ann. Physik*, 1924, **13**, 599). Rydberg series are only likely for the excitation of lone-pair electrons (or, sometimes, of weakly bonding or anti-bonding electrons); excitation of an electron from a strongly bonding orbital is hardly likely to give a series of discrete transitions. For this reason it seems best to interpret the first and third limits as due respectively to ionization from the (b_1) and (a_1) lone-pair orbitals; leaving the second limit to represent ionization of the (b_2) bonding electrons. The ground state configuration of H_2O is therefore written as $(a_1)^2(a_1)^2(b_2)^2(b_1)^2$ instead of $(a_1)^2(b_2)^2(a_1)^2(b_1)^2$. The main conclusions of this paper would not, however, be altered if the order of the (a_1) and (b_2) orbitals were reversed.*

Two intra-valency-shell orbitals other than those shown in the Figure are possible. These are highly anti-bonding in nature, being obtained by considering out-of-phase overlap of an oxygen valency with the hydrogen 1*s* valency. The lower of the two is of

* Price and Sugden (*loc. cit.*) assume that (b_2) is more tightly bound than (a_1).

species $\bar{a}_1$–σ_g, where the bar indicates the anti-bonding nature. For spectroscopic purposes it must be considered as non-localized and therefore built by the in-phase overlap of the two hydrogen 1*s* atomic orbitals, these interacting out-of-phase with an oxygen valency that is 2*s* in the linear molecule and $2p_z$ in the 90° molecule. Because of its anti-bonding nature, it may well lie so high that transition to it requires as much energy as transition to the lowest extra-valency-shell (Rydberg) orbital. In other words, the longest wave-length allowed transition of H_2O may be formulated

$$(a_1)^2(a_1)^2(b_2)^2(b_1)(a_1),^1B_1 \longleftarrow (a_1)^2(a_1)^2(b_2)^2(b_1)^2,^1A_1$$

where the uppermost (a_1) orbital refers either to the anti-bonding intra-valency-shell orbital or to the 3*s* orbital of the oxygen atom. The 1830—1500-Å absorption has already been interpreted as due to transition of an electron from (b_1) to $(3sa_1)$ (Mulliken, *J. Chem. Phys.*, 1935, **3**, 506; Price, Teegan, and Walsh, *Proc. Roy. Soc.*, 1950, *A*, **201**, 600). Its continuous nature, however, makes it best considered as involving also transition to a repulsive upper state containing an electron in the anti-bonding $(\bar{a}_1)$ orbital (cf. Walsh, unpublished work).

According to Wilkinson and Johnston (*J. Chem. Phys.*, 1950, **18**, 190) the absorption actually consists of three diffuse bands superimposed on a continuum. Rathenau (*Z. Physik*, 1934, **87**, 32) had earlier found structure in the continuum, stating that a frequency difference ~1300 cm.$^{-1}$ was present. The diffuse bands found by Wilkinson and Johnston are at 1608, 1648, and 1718 Å. It is possible that they represent the Rydberg transition while the continuum represents the intra-valency-shell transition. The maximum molecular extinction coefficient is about 1000.* It seems therefore that the transition(s) must be regarded as allowed, in agreement with the present assignments. Because of this, one expects either or both of the two totally symmetrical vibrational frequencies of the upper state to appear in the spectrum. It is possible that the separation of the 1608 and the 1648 Å band (1520 cm.$^{-1}$) represents the bending vibration ν_2 (1595 cm.$^{-1}$ in the ground state), and that the separation of the 1608 and the 1718 Å band (3388 cm.$^{-1}$) represents the stretching vibration ν_1 (3655 cm.$^{-1}$ in the ground state). The smallness of the reductions in these frequencies from the ground-state values would accord with only one quantum of each vibration appearing. It seems that comparatively little change of the molecular dimensions occurs on excitation, in agreement with the transition being of an electron from one non-bonding orbital (whose binding energy changes little with change of HOH angle) to another.

(ii) *Spectrum of* NH_2. In the ground state of the NH_2 radical only one electron lies in the (b_1) orbital. A long-wave-length transition

$$\cdots(a_1)(b_1)^2,^2A_1 \longleftrightarrow \cdots(a_1)^2(b_1),^2B_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

should therefore be possible. It represents an allowed transition. The further, long-wave-length, transition

$$\cdots(b_2)(b_1)^2,^2B_2 \longleftrightarrow \cdots(b_2)^2(b_1),^2B_1$$

is forbidden. The allowed transition should be polarized in the *x* direction, *i.e.*, perpendicularly to the molecular plane. Since the transition involves transfer of an electron from the orbital represented in the Figure by the steep a_1–π_u curve to the orbital represented by the approximately horizontal b_1–π_u line, it should result in an increase of the apex angle in the equilibrium form of the upper state. On the other hand, since the (a_1) and the (b_1) orbital are non-bonding, there should be little change of N–H length.

The so-called " ammonia α " band, lying in the visible region, has long been attributed (though without proof) to the NH_2 radical. It was first observed by Eder (*Denkschr.*

* Wilkinson and Johnston record intensities in terms of the atmospheric absorption coefficient at 30° c. Their values have been multiplied by (22·4 × 303)/(2·30 × 273) in order to obtain molecular extinction coefficients. The present discussion assumes that the bands observed by them in the continuum are not due to impurities. There is some doubt of this, however, since Rathenau's findings are not entirely in agreement with those of Wilkinson and Johnston.

Wien. Akad., 1893, **60**, 1) in the ammonia–oxygen flame. It was later found to occur (more weakly) in the spectrum of an uncondensed discharge through ammonia (Rimmer, *Proc. Roy. Soc.*, 1923, *A*, **103**, 696). The latter method of obtaining it supports the identification of the emitter as a decomposition product of NH_3. The band also occurs in the spectra of the hydrogen–nitrous oxide (Fowler and Badami, *ibid.*, 1931, *A*, **133**, 325; Gaydon, *ibid.*, 1942, *A*, **181**, 197) and the methane–nitrous oxide flames (Gaydon, *loc. cit.*). Infra-red bands observed in the spectrum of the former flame have been provisionally assigned to an extension of the band (Gaydon, *loc. cit.*). Rimmer's high-resolution photographs showed the great complexity of the band and the many lines (some 3000) present. The fine structure appears much too complex for the emitter to be the diatomic radical NH. Its attribution to NH_2 therefore seems very plausible. If the attribution is correct, then the interpretation of the band can hardly be other than as the emission transition (3). Analysis of the observed rotational structure should proceed in the light of the expectations formulated above.* That the structure should be so complex is not surprising (i) if the HNH angle is such that the molecule is not even an approximate symmetric top † and (ii) if, as expected here, the apex angle changes markedly in the transition.

(iii) *Spectrum of* CH_2. If the ground state of the molecule is a singlet, then the following is the longest-wave-length absorption transition :

$$K^2(a_1)^2(b_2)^2(a_1)(b_1),{}^1B_1 \longleftarrow K^2(a_1)^2(b_2)^2(a_1)^2,{}^1A_1$$

Mulliken (quoted by Venkateswarlu, *Phys. Review*, 1950, **77**, 676) has earlier made the same assignment. The transition is allowed, with polarization perpendicular to the main symmetry axis. It should probably occur at quite long wave-lengths (cf. the supposed NH_2 transition above). It would result in an increase of apex angle in the equilibrium form of the upper state. On the other hand, there should be little change of C–H length. The Figure thus enables very specific statements to be made about the expected spectrum of CH_2, which should be helpful in the search currently being undertaken in various laboratories for that spectrum.

It is worth noting what the expectations would be if the ground state of the CH_2 molecule should turn out to be a triplet. This implies that the molecule is nearly linear in the ground state and we shall therefore use the σ, π, $\cdots$ nomenclature for its orbitals. Consider only transitions with no change of multiplicity : the lowest energy transition, *viz.*,

$$(\sigma_g)^2(\sigma_u)(\pi_u)^2(\pi_u),{}^3\Pi_g \longleftarrow (\sigma_g)^2(\sigma_u)^2(\pi_u)(\pi_u),{}^3\Sigma_g^-$$

is forbidden. There will be no allowed transitions until comparatively short wave-lengths (probably, by analogy with H_2O, not until wave-lengths <2500 Å). The longest wave-length allowed transition will be ${}^3\Pi_u \longleftarrow {}^3\Sigma_g^-$ whose interpretation may be

$$(\sigma_g)(\sigma_u)^2(\pi_u)^2(\pi_u) \longleftarrow (\sigma_g)^2(\sigma_u)^2(\pi_u)(\pi_u) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or

$$(\sigma_g)^2(\sigma_u)^2(\pi_u)(\sigma_g') \longleftarrow (\sigma_g)^2(\sigma_u')^2(\pi_u)(\pi_u)$$

where (σ_g') stands for either the 3*s* carbon atom orbital or the anti-bonding orbital referred to above in the discussion of the H_2O spectrum.

If the CH_2 molecule is found to have a strong transition at wave-lengths considerably longer than 2500 Å, it should be safe to conclude that (*a*) the apex angle in the ground state is considerably less than 180° and (*b*) the ground state is a singlet.

* Since this paper was written, Dr. D. A. Ramsay has informed me that Professor Herzberg and he have now (*a*) proved that the ammonia α bands are due to NH_2, (*b*) obtained the system in absorption between 4500 and 7400 Å, and (*c*) shown, in agreement with the present expectations, that the upper and the lower state differ considerably in the geometrical arrangement of the nuclei (see Herzberg and Ramsay, *J. Chem. Phys.*, 1952, **20**, 347; *Discuss. Faraday Soc.*, 1953, **14**, 11). Dr. Ramsay has also pointed out to me that the same assignment of the bands as made here has been given earlier by Mulliken and quoted as a personal communication in a paper by Swings, McKellar, and Minkowski (*Astrophys. J.*, 1943, **98**, 142).

† According to the Figure the apex angle in the ground state should be close to that of the H_2O molecule.

Relation to Other Work.—In the following papers we shall show that, as with AH_2 molecules, the shape of a molecule in its ground state depends primarily on the number of valency electrons. In general terms, the recognition of this is of course not new (see, *e.g.*, Cassie, *Nature*, **1933**, **131**, 438; Penney and Sutherland, *Proc. Roy. Soc.*, **1936**, *A*, **156**, 654), though the newer data now available frequently enable the older generalizations to be extended and made more precise. There seems, however, to have been only one previous attempt to plot a correlation diagram between the orbitals possible for a polyatomic molecule in each of two nuclear configurations, and to use such a diagram to discuss both the shapes (in excited as well as ground states) and electronic spectra of molecules. This was by Mulliken (*Rev. Mod. Phys.*, **1942**, **14**, 204) who plotted a correlation diagram for the limited case of AB_2 molecules. He did not specifically apply his diagram to AH_2 molecules. He also said that he was unable to give any simple explanation of why particular curves should rise or fall with increase of angle. His diagram was either empirical or based upon unpublished computations.

UNIVERSITY OF LEEDS. [*Received, May 15th*, 1952.]

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467. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part II.* Non-hydride* AB_2 *and* BAC *Molecules.*

By A. D. WALSH.

A correlation diagram is plotted for the orbitals of linear and non-linear triatomic molecules. Simple reasons are given why particular orbitals become more or less tightly bound as the apex angle changes. The diagram is used to interpret and predict the shapes, reactivities, and spectra of non-hydride triatomic molecules. As regards the shapes, the following facts (most of which have been recognised for some time) become understandable: that molecules with not more than 16 valency electrons are linear in their ground states; that molecules with 17, 18, 19, or 20 valency electrons are bent in their ground states, the apex angle decreasing markedly from 16- to 17- and from 17- to 18-electron molecules and less markedly from 18- to 19- and from 19- to 20-electron molecules; and that 22-electron molecules are linear or nearly linear in their ground states. The paper has much in common with an earlier paper by Mulliken.

THE purpose of this paper is to apply to AB_2 and BAC molecules the procedure which in Part I * was applied to AH_2 molecules. We consider first symmetrical, non-hydride, triatomic molecules AB_2.

AB_2 *Molecules.*—The lowest-energy orbitals of a linear AB_2 molecule may, on the assumption that they are built solely from *s* and *p* atomic orbitals, be described as follows: (i) Two lone-pair *s* orbitals, one on each B atom. (ii) Two bond orbitals analogous to the bond orbitals discussed in Part I. For discussion of molecular shape, they may be thought of as built from *sp* hybrid valencies of A plus $p\sigma$ valencies of the two B atoms and largely localized one to each A–B distance. In discussion of spectroscopic transitions involving them, they would have to be regarded as non-localized combinations of the localized orbitals and be labelled σ_g and σ_u. (For simplicity, hybridization of the *s* and the *p* valencies of the B atoms is here neglected. It is unlikely that its inclusion would alter the general form of the correlation diagram plotted in the Figure. A similar comment applies to later papers of this series.) (iii) A π_u orbital built by the in-phase overlap of a $p\pi$ atomic orbital on each of the three atoms. It will be bonding and two-fold degenerate. (iv) A π_g orbital built by the out-of-phase overlap of a $p\pi$ atomic orbital on each of the B atoms. It has zero amplitude at the central atom, being localized entirely on the B atoms. It is two-fold degenerate, weakly B$\leftrightarrow$B anti-bonding and A$\leftrightarrow$B non-bonding. (v) A $\bar{\pi}_u$ orbital built by the in-phase overlap of a $p\pi$ atomic orbital on each of the B atoms,

* Part I, preceding paper.

these overlapping out-of-phase with a $p\pi$ orbital on the central atom. It is two-fold degenerate, B$\longleftrightarrow$B bonding and A$\longleftrightarrow$B anti-bonding. A bar is placed over the symbol to indicate the A$\longleftrightarrow$B anti-bonding nature.

The π_u orbitals are both built from atomic orbitals on each of the three atoms. Nevertheless they will be partly localized in a way that may be deduced as follows. The sharing of an electron between two atomic orbitals is only likely when those two atomic orbitals have equal, or almost equal, binding energy. If the two atomic orbitals differ widely in binding energy no sharing will take place. It follows that if the $p\pi$ atomic orbitals of A are *much* less tightly bound than those of B the possible π orbitals in the molecule AB_2 are as follows: two orbitals (each two-fold degenerate) practically entirely localized on the B atoms and one higher-energy orbital (also two-fold degenerate) practically entirely localized on the A atom. In most actual AB_2 molecules (*e.g.*, CO_2, SO_2, OF_2, NO_2), B has considerably greater electronegativity (*i.e.*, has considerably more tightly bound valency orbitals) than A. While therefore it would be too extreme to speak of complete localization of any of the π orbitals, it follows that the three two-fold degenerate π-orbitals fall into two groups: (*a*) the two lower-energy ones (π_u and π_g) which should be more localized on the B than on A atoms, and (*b*) the higher-energy $\bar{\pi}_u$ orbital which should be more localized on A than on the B atoms. In the case of the π_g orbital, this argument merely reinforces what was already evident from the nature of the orbital [see (iv) above]. In the non-linear molecule the degeneracy of each of the orbitals is split. The π_u orbitals each yield an a_1' and a b_1'' orbital while the π_g orbital yields an a_2'' and a b_2' orbital. The primes are added for clarity to the usual group-theory symbols. A single prime means that the orbital is symmetric with respect to reflection in the plane of the molecule, a double prime that it is anti-symmetric. (vi) A $\bar{\sigma}_g$ orbital which is similar to the $\bar{\sigma}_g$ orbital described in Part I in the discussion of the spectrum of H_2O. It is built by the in-phase overlap of a $p\sigma$ valency on each of the B atoms, these overlapping out-of-phase with an *s* atomic orbital on the central atom. It is A$\longleftrightarrow$B anti-bonding, though B$\longleftrightarrow$B bonding.

In AH_2 molecules, there is general agreement that the π_u lies below the $\bar{\sigma}_g$ orbital. This is likely because the former is non-bonding whereas the latter is A$\longleftrightarrow$H anti-bonding. In non-hydride, AB_2 molecules, however, the orbital corresponding to π_u of AH_2 is $\bar{\pi}_u$, *i.e.*, an orbital that is A$\longleftrightarrow$B anti-bonding. A major reason for the orbital's lying lower than $\bar{\sigma}_g$ is therefore removed. We shall see in discussing the spectra of AB_2 molecules, however, that there is no compelling evidence for $\bar{\sigma}_g$ not still lying above $\bar{\pi}_u$.

By arguments similar to those given above, the $\bar{\sigma}_g$ orbital is more localized on the A than on the B atom.

The lowest-energy orbitals of a 90° AB_2 molecule may then be described as follows.

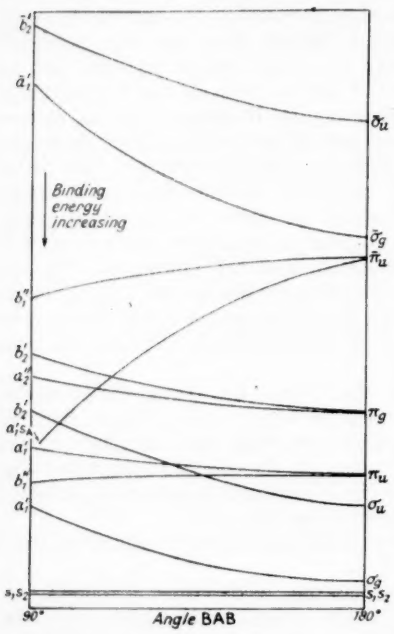
(i) Two lone-pair *s* orbitals, one on each B atom. It is assumed that these play little part in the binding of the B to the A atoms and that, being rather more tightly bound than any of the other valency orbitals of B or than any of the valency orbitals of A, they vary little in energy as the apex angle changes from 90° to 180°. They are therefore represented by horizontal straight lines on the correlation diagram (see Figure).

(ii) Two bond orbitals. Considered as localized orbitals, they are built from pure *p* valencies of the A atoms overlapping with *p* valencies of the B atoms. Considered as non-localized orbitals, their symbols are a_1' and b_2'. As described in Part I they both become more tightly bound as the apex angle changes from 90° to 180°.

(iii) An $a_1 s_A$ orbital. This, in first approximation, is a pure *s* orbital localized on atom A. As the apex angle changes from 90° to 180° this must, as described in Part I, tend to go over into a $p\pi$ orbital localized on atom A. It must therefore tend to correlate with the upper rather than with the lower π_u orbital. The localization on atom A was complete for AH_2 molecules. For AB_2 molecules the orbital will be largely, but not completely, localized on A. The curve representing the orbital rises steeply from left to right on the correlation diagram (Figure). The steep rise may be accentuated because the orbital becomes markedly A$\longleftrightarrow$B anti-bonding in the linear molecule. The Figure thus incorporates largely unchanged three of the curves of the Figure in Part I.

(iv) Three orbitals anti-symmetrical with respect to reflection in the plane of the

molecule. The first of these (b_1'') is built from a p atomic orbital on each of the three atoms overlapping in-phase. It is A←→B and (weakly) B←→B bonding, and becomes one of the lower π_u orbitals in the linear molecule. The A atomic orbital concerned in it is pure p in both bent and linear molecules. According to the principles enunciated in Part I any change of binding energy as the apex angle is changed is therefore governed by the fact that it is weakly B←→B bonding. This means it will be rather more stable (lead to more evolution of energy) when the two B atoms are as close together as possible (*i.e.*, in the 90° molecule). The curve representing the orbital in the Figure has therefore been drawn to rise slightly from left to right. The second of these orbitals (a_2'') is built from a p atomic orbital on each of the B atoms overlapping out-of-phase. It is A←→B non-bonding and B←→B anti-bonding, and becomes one of the π_g orbitals in the linear molecule. Because it is B←→B anti-bonding it will be more stable when the two B atoms are as far apart as possible (*i.e.*, in the 180° molecule). The curve representing the orbital in the Figure has therefore been drawn to decrease from left to right. The third orbital (b_1'') is built from a p atomic orbital on A overlapping out-of-phase with each of two p orbitals, one on each of the B atoms. In a 60° B_3 molecule this b_1'' orbital would be degenerate with the a_2'' orbital. It is the analogue of the b_1 orbital shown in the Figure of Part I. Because of the presence of low-lying p atomic orbitals on the B atoms it is now, however, A←→B anti-bonding and B←→B bonding, instead of non-bonding and localized solely on A. Because it is B←→B bonding it will be most stable when the two B atoms are as close together as possible. It is represented in the Figure therefore, not by an horizontal line (as in Part I), but by a line that rises from left to right.



(v) Two orbitals symmetrical with respect to reflection in the plane of the molecule and primarily built from two p atomic orbitals lying one on each B atom with axes in the molecular plane and at right angles to the direction of the adjacent B–A line. That which involves in-phase overlap of these two orbitals is of species a_1'. That which involves out-of-phase overlap is of species b_2'. The a_1' orbital becomes one of the lower π_u orbitals in the linear molecule. It is B←→B bonding, which supplies a reason why it should decrease in binding energy with increase of apex angle. On the other hand, because the s orbital on A is expected to interact little with the p orbitals on the B atoms from which a_1' is built, in the 90° molecule the a_1' orbital largely loses the A←→B bonding character which it has in the linear molecule. This supplies a reason why the a_1' orbital should become more tightly bound as the apex angle increases. The a_1' orbital has therefore been inserted in the Figure as showing comparatively little dependence on angle.* The b_2'–π_g orbital is B←→B anti-bonding and is therefore represented in the Figure by a line that falls from left to right.

(vi) An $\bar{a}_1'$ orbital that correlates with the $\bar{\sigma}_g$ orbital of the linear molecule. This

* As a net effect the a_1' orbital curve probably falls from left to right in the Figure for the following reason. In a 60° B_3 molecule the a_1' orbital leading to the upper π_u should become degenerate with the b_2' orbital leading to π_g. This might happen if the a_1' orbital leading to the lower π_u curls upwards from right to left. For if orbital curves of the same species cannot cross, the a_1' orbital curve leading to the upper π_u may contain a minimum to the left of which it curves steeply upward to meet the b_2' orbital. It should be emphasized, however, that it is the part of the diagram from 90° to 180° that concerns real molecules.

orbital consists largely of an A atomic orbital. According to the principles given in Part I, it is built from a p_z orbital of A in the 90° molecule but from an *s* orbital of A in the 180° molecule; and therefore is represented in the Figure by a line that falls steeply from left to right.

If it should happen that the $\bar{\sigma}_g$ orbital lies *below* $\bar{\pi}_u$, then the curve from the $a_1's_A$ orbital will lead, not to the $\bar{\pi}_u$, but to the $\bar{\sigma}_g$ orbital. Orbital curves of the same species cannot cross.* In that case, the steep rise over most of its course of the curve from the $a_1's_A$ orbital could still be regarded as due to the reasons already described, *i.e.*, to its "trying" to reach $\bar{\pi}_u$; but an "avoided crossing" would have to be drawn, with the result that the curve from the $\bar{a}_1'$ orbital which "tended" to proceed to $\bar{\sigma}_g$ would be drawn in fact to proceed to the $\bar{\pi}_u$ orbital. However, we shall see below that the balance of evidence is not unfavourable to $\bar{\sigma}_g$ lying above $\bar{\pi}_u$, *i.e.*, no such "avoided crossing" is necessary.

(vii) A total of twelve intra-valency-shell orbitals can be built from one *s* and three *p* atomic orbitals on each of the three atoms of AB_2. For completeness therefore a twelfth orbital curve has been added to the Figure. It represents a $\bar{b}_2'$–$\bar{\sigma}_u$ orbital which is built by the out-of-phase overlap of valencies on the B atoms, these themselves overlapping out-of-phase with a *p* valency of A. It is A⟷B and B⟷B anti-bonding. Because it involves no change of A valency as the apex angle is changed and is B⟷B anti-bonding, it is represented in the Figure by a curve that falls from left to right. It may well lie so high in energy, however, that it is above the lowest extra-valency-shell orbital.

It should be emphasized (1) that the actual forms of the curves in the Figure are uncertain, except that each must be a maximum or minimum on the 180° line, (2) that though the energy order of the orbitals on the 180° ordinate is probably definite (except perhaps for $\bar{\sigma}_g$ and $\bar{\pi}_u$) † that of the orbitals on the 90° ordinate is uncertain, (3) that no stress should be put upon the quantitative energy differences shown even on the 180° ordinate,‡ and (4) that though the above arguments provide plausible support for the rise or fall from left to right of a given orbital they are not always conclusive. In other words, some of the support for much in a correlation diagram such as that illustrated must be empirical. We therefore proceed below to examine how far the Figure can explain known facts.

BAC *Molecules.*—A diagram very similar to the Figure for AB_2 molecules should also hold for BAC molecules. The absence of a centre of symmetry now means that the *g* and *u* suffixes for the orbitals in the linear molecule must be abandoned. With the exception of the primes, the symbols for the bent molecule (C_s symmetry) also become inappropriate. The only appropriate symbols are now *a'* and *a''*.

Shapes of Non-hydride, Triatomic Molecules.—Of the lowest eight orbital curves on the right-hand side of the Figure, all but one either decrease from left to right or are horizontal. The one exception rises only slightly from left to right. One therefore expects that AB_2 or BAC molecules containing 16 or less valency electrons will be linear in their ground states. So far as is known there are no exceptions to this rule. CO_2, COS, CS_2, N_2O, ClCN, $HgCl_2$, NCO^-, and N_3^- supply well-known examples. Of less well-known molecules, the ions CO_2^+ (see below) and NO_2^+ (see Gillespie and Millen, *Quart. Reviews*, **1948**, **2**, 277) are linear, while the radicals C_3 and N_3 would be expected to be linear. The uranium atom has six valency electrons, the configuration in the ground state being $\cdots(5f)^4(7s)^2$, where the (5*f*)- and the (7*s*)-orbitals have closely similar binding energies. One would expect, therefore, that the ion UO_2^{++} would be linear in the ground state. This is true (Zachariasen, *Acta Cryst.*, **1948**, **1**, 277, 281; Sutton, *Nature*, **1952**, **169**, 235). It seems

* The point is the same as that involved in the familiar diagrams correlating the orbitals of two separated atoms with those of the united atom. "The lowest σ orbital to the right goes into the lowest σ orbital to the left, the second lowest σ orbital to the right goes into the second lowest to the left and so on" (Herzberg, "Molecular Spectra and Molecular Structure," Van Nostrand, New York, 1950, p. 327).

† For CO_2 the ionization energies for electrons in the σ_u, π_u, and π_g orbitals are known to be 18·00, 17·32, and 13·79 ev.; *i.e.*, the σ_u lies only just below the π_u orbital, the π_g orbital lying considerably higher, in accord with the Figure.

‡ In any case these energy differences must vary from molecule to molecule.

that the implications of the Figure are not limited to light atoms but apply throughout the Periodic Table. The ions $AgCl_2^-$ and $AuCl_2^-$ are linear.* One may deduce, either directly by arguments similar to those of this paper or by analogy with the isoelectronic CO_2 that the ground states of keten and allene molecules will have linear CCO or CCC chains respectively.

The ground state of a molecule such as NO_2, however, containing 17 valency electrons, has to have its outermost electron in the $a_1's_A$–$\bar{\pi}_u$ orbital which rises steeply from left to right in the Figure. The ground state of the NO_2 molecule is therefore bent,† its apex angle showing a considerable drop from 180°. When NO_2^+ reacts, a donation of electrons to it may be considered to occur. These electrons occupy the $a_1's_A$–$\bar{\pi}_u$ orbital, resulting in the NO_2 group's becoming triangular. NO_2 is the only 17-electron molecule for which an apex angle has been reported. Two rather widely different values for this angle have been given (Table 1). The mean drop from 180° is 37° ± 11°. One would expect the apex

TABLE 1. *Apex angles of ground states of triatomic molecules.*

No. of valency electrons	Molecule	Apex angle	Ref.	Mean value	Method of determn.
16	Numerous	180°		180°	—
17	NO_2	154 ± 4	*a*	143 ± 11	Electronic spectrum
		132 ± 3 *	*b*		Electron diffraction
18	NOCl	116	*c*		,, ,,
	NOBr	117	*c*		,, ,,
	NO_2^- (in crystal)	114 ± 4	*d*		*X*-Ray diffraction
		115	*e*	117	,, ,,
	O_3	127 ± 3	*f*		Electron diffraction
		116·5—117	*g*		Micro-waves
	SO_2	119° 2′	*h*		,,
19	ClO_2	116·5°	*i*	116·5	Electron diffraction
20	F_2O	101	*j*		,, ,,
	Cl_2O	110·8	*i*		,, ,,
	Cl_2S	101 ± 4	*k*	103	,, ,,
		103 ± 3	*l*		,, ,,
	Br_2Te	98 ± 3	*m*		,, ,,
22	$BrIBr^-$		*n*		*X*-Ray diffraction
	$ClICl^-$	180° or	*o*	180	,, ,,
	I_3^-	*ca.* 180°	*p*		,, ,,
	$ClIBr^-$		*q*		,, ,,

* Spurr, using the electron diffraction data of Maxwell and Mosley (*J. Chem. Phys.*, 1940, **8**, 738), found 141° (quoted by Jost and Russell, "Systematic Inorganic Chemistry," Prentice Hall, New York, 1944).

[a] Harris and King, *J. Chem. Phys.*, 1940, **8**, 775. [b] Claesson, Donohue, and Schomaker, *ibid.*, 1948, **14**, 207. [c] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629. [d] Truter, personal communication; Mrs. Truter (*Nature*, 1951, **168**, 344) originally reported the angle as 132° 48′, but has since revised her estimate. [e] Carpenter, *Acta Cryst.*, 1952, **5**, 132. [f] Shand and Spurr, *J. Amer. Chem. Soc.*, 1943, **65**, 179. [g] Hughes, *Bull. Amer. Phys. Soc.*, 1951, **26**, 21, No. 6. [h] Crable and Smith, *J. Chem. Phys.*, 1951, **19**, 502. [i] Dunitz and Hedberg, *J. Amer. Chem. Soc.*, 1950, **72**, 3108. [j] Brockway, *Rev. Mod. Phys.*, 1936, **8**, 231. [k] Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360. [l] Stevenson and Beach, *ibid.*, p. 2872. [m] Rogers and Spurr, *ibid.*, 1947, **69**, 2102. [n] Bozorth and Pauling, *ibid.*, 1925, **47**, 1561. [o] Wyckoff, *ibid.*, 1920, **42**, 1100. [p] Mooney, *Z. Krist.*, 1935, **90**, 143. [q] Mooney, *Phys. Review*, 1935, **47**, 807; *Z. Krist.*, 1938, **98**, 324; 1939, **100**, 519.

angle to show a further marked drop if an eighteenth electron were added. The exact value of the apex angle in 18-electron molecules must vary from molecule to molecule because the heights of the various orbitals and the steepness of their change with angle must vary from molecule to molecule. In other words, if it ever becomes possible to plot the Figure in a completely quantitative way, a separate figure really needs to be plotted for each molecule. It is remarkable, however, that the apex angles reported for various

* The hybrid valencies giving linearity may not be *sp* when heavy elements are considered. The general ideas of the present argument should, however, still be valid.

† *Added in Proof.*—It is not obvious that *one* electron in the $a_1's_A$–$\bar{\pi}_u$ orbital should outweigh the effect of, *e.g.*, the filled a_1–σ_g and b_2–σ_u orbitals. However, the fall of the a_1–σ_g curve from left to right in the Figure is offset by the B ⟷ B bonding nature of the orbital; whereas the rise of the $a_1's_A$–$\bar{\pi}_u$ curve is accentuated by the B ⟷ B bonding nature of the orbital and by its becoming A ⟷ B anti-bonding in the linear molecule. It is plausible therefore that the latter curve should rise much more steeply than the a_1–σ_g curve falls. See also the footnote concerning this point on p. 2263.

18-electron molecules only vary over a range (*ca.* 12° at most and probably only 5°) that is small compared with the total range of the abscissa in the Figure.* These angles are given in Table 1. The mean value implies a drop of *ca.* 26° from the mean value for NO_2. A 19-electron molecule has to place its outermost electron in the b_1'–$\bar{\pi}_u$ orbital. Since the curve of this orbital rises from left to right in the Figure, but not as steeply as that of the $a_1's_A$–$\bar{\pi}_u$ orbital, one would expect the apex angle of such a molecule to show a further, but smaller, drop from the value characteristic of 18-electron molecules. The only 19-electron molecule for which an apex angle has been reported is ClO_2. The value of the angle reported for this molecule probably has a considerable uncertainty, but is not incompatible with the expected small drop from the mean value for the 18-electron molecules. One would expect a further small drop in the apex angle of a 20-electron molecule. One expects and finds the actual angle reported for such molecules to cover a range of values, but again the range is small (*ca.* 13°: see Table 1). The mean value represents a drop of about 13° from the value for ClO_2.

To sum up, all 17-, 18-, 19-, and 20-electron molecules have ground states that are bent; the apex angle drops considerably from 16- to 17-electron molecules; and also from 17- to 18-electron molecules; the apex angle also drops, but less markedly, from 18- to 19-electron molecules and from 19- to 20-electron molecules; and these facts fit very well with expectations from the Figure. It is remarkable that mere number should determine, for AB_2 and BAC as for AH_2 molecules, the crude magnitude of the apex angle (cf. Cassie, *Nature*, 1933, **131**, 438; Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 654; Sidgwick and Powell, *ibid.*, 1940, *A*, **176**, 153).

The first excited state of the CO_2 molecule has its most weakly bound electron in the $a_1's_A$–$\bar{\pi}_u$ orbital. It has the same reason as the ground state of NO_2 for being bent, and at the same time has one less electron in the orbitals stabilizing the linear form. One strongly expects therefore the first excited state of CO_2 to be bent. We discuss evidence in favour of this below. The keten and the allene molecule are isoelectronic with CO_2. It follows either directly by arguments similar to those of this paper, or by analogy with CO_2, that the CCO or CCC chains in the equilibrium forms of the lowest-lying excited states of these molecules should be non-linear (cf. Sutcliffe and Walsh, *J.*, 1952, 899). Further examples of molecules which have linear ground states but probably bent upper states are given in a discussion below of the spectra of triatomic molecules. It is probably a very common phenomenon for polyatomic molecules to have different shapes in their excited and in their ground states (cf. the following papers).

The ground state of a 22-electron molecule must have two electrons in the $\bar{a}_1' - \bar{\pi}_u$ orbital. The trend of the apex angle in 16—20-electron molecules should therefore be sharply reversed on proceeding further to 22-electron molecules. Indeed, if the $\bar{a}_1'$–$\bar{\pi}_u$ curve falls sufficiently steeply, 22-electron molecules should be linear in their ground states. As Table 1 records, the trihalide ions are reported, experimentally, to be linear or nearly so. Pimentel (*J. Chem. Phys.*, 1951, **19**, 446) has earlier discussed the molecular orbitals involved in the ground states of trihalide ions, accepting these states as linear, but he made no attempt to discuss the more difficult problem of why this was so. In essentials Pimentel's conclusions agree with the orbitals that would be predicted from the Figure for the ground state of a 22-electron molecule. In particular agreement with Pimentel, the Figure shows that there is no need to invoke the use of *d* orbitals to explain (qualitatively) the bonding (and the linearity) of the trihalide ions.

Alternative Statement of the Factors determining the Apex Angle.—It is striking that the apex angles of the ground states of H_2O and F_2O are nearly the same (104° and 101° respectively).† It presumably means that H–H and F–F repulsions are of minor importance in determining the angle. This is readily interpreted in terms of the Figure. The major factors determining the apex angle lie in the a_1'–σ_g, b_2'–σ_u, and a_1s_A–$\bar{\pi}_u$, curves, *i.e.*, in the curves largely common to the Figures of the preceding and of the present paper. It can be seen from the Figure that the sum of the b_1''–$\bar{\pi}_u$, b_2'–π_g, a_2''–π_g, a_1'–π_u, and

* Similarly, it was pointed out in Part I that the known angles for 8-electron AH_2 molecules vary only over a range of 14°.

† I am indebted to Dr. P. Torkington for stressing this to me.

b_1''–π_u curves changes comparatively little with the angle. The major changes in binding energy with angle may therefore be regarded as due to the three remaining curves which, for F_2O, must be substantially the same as for H_2O. In other words, the major factor determining the apex angle is a property of the central atom. It is the interaction between the valencies of this atom used for the bonding orbitals and the lone pair a_1' orbital.

So far we have expressed this interaction in terms of hybridization of the valencies of the central atom. One could express the interaction in alternative terms of electrostatic repulsions between the electrons in the bond orbitals and those in the "lone-pair" orbital (cf. Pople, *Proc. Roy. Soc.*, 1950, *A*, **202**, 323). Thus the fundamental reason why 17- and 18-electron molecules have ground states that are bent is because they have 1 and 2 electrons respectively which are in orbitals more localized on the central than on the end atoms and repel the bond electrons. As a consequence of the molecule's bending, the extra electrons come to occupy an orbital whose contribution from the central atom is no longer pure p, but an sp hybrid pointing in the $+z$ direction (axes as in Part I). At the same time the valencies of the central atom used for the bond orbitals become more nearly pure p, *i.e.*, become less electronegative (Walsh, *Discuss. Faraday Soc.*, 1947, No. 2, p. 18). The hybridization changes thus imply that the electrons in the lone-pair orbital move away from the bond orbitals in the z direction (the orbital no longer having its centre of gravity at the nucleus of A as it had in the linear molecule) while the bond electrons move away from atom A towards atoms B. These are just the changes expected to follow from repulsion between lone-pair electrons on A and the bond electrons.

In the ground states of 22-electron molecules, two electrons are placed in a further orbital which is more localized on atom A than on atoms B. This orbital is built from a p_z orbital of A in the 90° molecule and from a pure s orbital of A in the linear molecule. At intervening angles the orbital represents the second sp hybrid that can be formed from the s and p_z orbitals of A. This second sp hybrid points in the $-z$ direction and so restores symmetry to the electron cloud around A. The bond electrons are now subject to repulsions from the electrons in the sp hybrids which tend to cause bending in opposite directions; thus the molecule resumes a linear or nearly linear form.

The key curves causing the major changes of shape are: (a) the bond orbital curves; (b) the $a_1's_A$–$\bar{\pi}_u(p_z)$ curve; and (*c*) the $\bar{a}_1'(p_z)$–$\bar{\sigma}_g(s_A)$ curve.

Reactivity of Triatomic Molecules.—The outermost, unpaired electron of the ground state of the NO_2 molecule lies in the $a_1's_A$–$\bar{\pi}_u$ orbital. From the arguments above, this electron is more localized on the N atom than on the O atoms. Reaction of NO_2 with a free radical is therefore likely to form a nitro-compound rather than a nitrite. Inhibition of certain free-radical reactions by NO_2 may plausibly be attributed to such reaction: the inhibition occurs under conditions where addition of a nitro-compound has no effect, but addition of a nitrite catalyses the reaction. Similarly, initiation of chains by H-abstraction by NO_2 (see, *e.g.*, McDowell and Thomas, *Trans. Faraday Soc.*, 1950, **46**, 1030) is likely to form $H{\cdot}N\langle^{O}_{O}$ rather than HO·NO. One might expect that, since NO_2 molecules readily associate to form N_2O_4, the latter molecule has the structure $O_2N{\cdot}N\langle^{O}_{O}$ (cf. Ingold and Ingold, *Nature*, 1947, **159**, 743; Walsh, *J. Chem. Phys.*, 1947, **15**, 688; Claesson, Donohue, and Schomaker, *ibid.*, 1948, **16**, 207; Broadley and Robertson, *Nature*, 1949, **164**, 915). On arguments similar to those given here, the outermost, unpaired electron of the ground state of the NO molecule is more localized on the N than on the O atom. Since NO and NO_2 associate to form N_2O_3, a certain presumption is raised in favour of the structure $O{-}N{\cdot}N\langle^{O}_{O}$ for N_2O_3 (see also Part V of this series).

The nitrite ion has its two most weakly bound electrons in the $a_1's_A$–$\bar{\pi}_u$ orbital, *i.e.*, more localized on the N atom than on the O atoms. One might therefore expect reaction with an acceptor entity to take place at the N atom rather than at the O atoms. In agreement, the nitrite ion reacts with a carbonium ion to form a nitro-compound (Austin, Thesis, London, 1950).

The ClCO radical has its outermost, unpaired electron more localized on the C than on

the Cl or O atom. One therefore expects it to react most readily at the C atom. This is in agreement with the reaction that has been postulated for the radical (Rollefson and Montgomery, *J. Amer. Chem. Soc.*, 1933, **55**, 142, 4025), namely, formation of carbonyl chloride : $Cl_2 + ClCO = Cl_2CO + Cl$.

The first excited state of the SO_2 molecule contains one electron in the $a_1'{}^{s_A}$–$\bar{\pi}_u$ orbital and one in the b_1''–$\bar{\pi}_u$ orbital. Both these orbitals are more localized on the S atom than on the O atoms. It is interesting that photochemical reactions of SO_2, presumably involving this excited state, have been shown to form two bonds to the *S* atom (Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 382). Moffitt (*Proc. Roy. Soc.*, 1950, *A*, **200**, 414) has previously noted that the most weakly bound electrons of the ground state of the SO_2 molecule lie in an (a_1) orbital (here called $a_1'{}^{s_A}$) which is predominantly localized on the S atom; and that the oxidation (" donor ") reactions of SO_2 to form SO_3 or SO_2Cl_2 can therefore be readily understood.

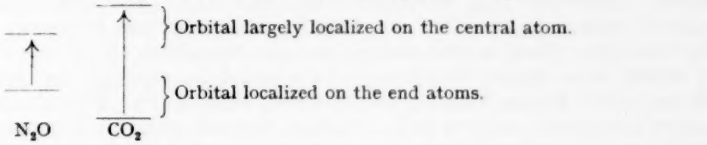
The discussion in this section is somewhat naive in that reactivity is a complicated matter; but it is sufficiently successful to suggest that the ideas involved are useful in considering not merely the ground state, but also the photochemical, reactions of molecules. Combined with the conclusions of the preceding section concerning the shapes of excited states, they should be of particular use in considering possible photochemical syntheses.

Relation to Other Work.—As mentioned in Part I, Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 204) has earlier plotted a correlation diagram for the orbitals of a linear and a bent triatomic molecule. Mulliken, however, was unable to give any simple reason why particular curves rose or fell with change of apex angle. In many respects, our Figure agrees with that of Mulliken. There are two major differences. The first is that Mulliken supposed $\bar{\sigma}_g$ to lie below $\bar{\pi}_u$ (for his reasons, see *J. Chem. Phys.*, 1935, **3**, 739). As already explained, this results in the curve from $a_1'{}^{s_A}$ leading to $\bar{\sigma}_g$ instead of to $\bar{\pi}_u$ and in the curve from $\bar{a}_1'$ leading to $\bar{\pi}_u$ instead of to $\bar{\sigma}_g$. The second major difference is that Mulliken drew the curve from $\bar{a}_1'$ as rising from left to right, whereas in the present Figure it has the opposite curvature. Mulliken's diagram made the reported linearity of the 22-electron molecules incomprehensible

Mulliken particularly used his diagram to interpret observed spectra of triatomic molecules. In the next section we give a fuller discussion of these observed spectra, indicating our agreement with, or changes from, Mulliken's assignments.

Spectra of Non-hydride, Triatomic Molecules.—(i) CO_2 *and* N_2O. It is striking that, whereas the N_2O and CO_2 molecules are isoelectronic, ultra-violet absorption by the former begins at *ca.* 3000 Å whereas that by CO_2 does not occur until *ca.* 1700 Å.* A simple explanation is as follows. The lowest-energy transition of these molecules, according to the Figure, is of an electron from the π_g to the $\bar{\pi}_u$ orbital. In other words, it is from an orbital largely localized on the end atoms to one largely localized on the central atom. The orbital localized on the end atoms will be less tightly bound in NNO than in OCO since the electronegativity of N is less than that of O.† On the other hand, the orbital largely localized on the central atom will be more tightly bound in NNO than in OCO since the electronegativity of N is greater than that of C. We have therefore the situation represented diagrammatically below and the transition in N_2O should require considerably less energy than that in CO_2.

The first electronic transitions of N_2O *and* CO_2.



According to our Figure (p. 2268) the upper state of the longest-wave-length-absorption

* Even in liquid CO_2 no absorption occurs until at least 2150 Å.

† It is easily seen that in N_2O the analogue of the lower π_u orbital is predominantly localized on the O atom, while the analogue of the π_g orbital is predominantly localized on the end N atom.

system of CO_2 should be related to the configuration $(\pi_g)^3(\bar{\pi}_u)$. This gives rise to $^1\Delta_u$ (two-fold degenerate), $^1\Sigma_u^-$, and $^1\Sigma_u^+$ states. By analogy with atoms and diatomic molecules one would expect $^1\Delta_u$ to be the lowest of these states. The transitions

$$\cdots(\pi_g)^3(\bar{\pi}_u),\quad {}^1\Delta_u \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (1)$$

and

$$\cdots(\pi_g)^3(\bar{\pi}_u),\quad {}^1\Sigma_u^- \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (2)$$

are forbidden; while

$$\cdots(\pi_g)^3(\bar{\pi}_u),\quad {}^1\Sigma_u^+ \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (3)$$

is allowed. Now, (3) should be a particularly intense transition since it belongs to the class of so-called "$V \longleftarrow N$" transitions which, compared with other intra-valency-shell transitions, are expected to have particularly high intensities (Mulliken, *J. Chem. Phys.*, 1939, **7**, 20). The different possible states correspond, in C_{2v} symbols, to the four configurations (see Figure)

$$(a_2'')^2(b_2')(a_1'),\quad {}^1B_2$$
$$(a_2'')(b_2')^2(a_1'),\quad {}^1A_2$$
$$(a_2'')^2(b_2')(b_1''),\quad {}^1A_2$$
$$(a_2'')(b_2')^2(b_1''),\quad {}^1B_2$$

The first two of these configurations represent states that are expected to be strongly bent, and the second two states that are expected to be slightly bent or linear. $^1\Delta_u$ correlates with $^1A_2$ and $^1B_2$; $^1\Sigma_u^+$ and $^1\Sigma_u^-$ correlate with $^1B_2$ and $^1A_2$ respectively. For bent upper states, the degeneracy of $^1\Delta_u$ is split, so that (1) has to be replaced by the two transitions

$${}^1A_2 \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (1A)$$

and

$${}^1B_2 \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (1B)$$

Both transitions would be weak, partly because forbidden by the Franck–Condon principle and partly because both are related to the forbidden transition (1). In addition, (1A) is forbidden by the symmetry-selection rules and has therefore an extra reason to be weak compared with (1B). Similarly, for bent upper states, (2) and (3) have to be replaced respectively by

$${}^1A_2 \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (2A)$$

and

$${}^1B_2 \longleftarrow \cdots(\pi_g)^4,\ {}^1\Sigma_g^+ \qquad (3A)$$

(2A) should be very weak because it is forbidden by the symmetry-selection rules and is related to the forbidden transition (2). Provided, however, that the upper state is not *strongly* bent, (3A) should be strong since it is allowed by the selection rules and is related to the intense transition (3).

The lowest-energy absorption of CO_2 falls into two regions, 1700—1400 and 1390—1240 Å. The latter region has $\lambda_{max.}$ at *ca.* 1335 Å (Price and Simpson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 501) and is much stronger than the 1700—1400-Å region, though not as strong as the Rydberg bands at shorter wave-lengths. There is no doubt that it represents an allowed intra-valency-shell transition. Indeed its intensity makes it only plausibly identified as transition (3) or (3A). In the latter case the upper state cannot be *strongly* bent. The appearance pressure of the 1390—1240-Å absorption, relative to the Rydberg bands, appears to be of the order found in other molecules for $V \longleftarrow N$, relative to Rydberg, transitions (*e.g.*, acetylene; see Part III). The 1700—1400-Å absorption contains a peak of $\varepsilon_{max.} \sim 110$ * (*ca.* 1495 Å; Wilkinson and Johnston, *J. Chem. Phys.*, 1950, **18**, 190). This is too strong for the transition to be plausibly interpreted as a triplet $\longleftarrow$ singlet transition (which would be expected to have an extinction coefficient < 1; Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 72). It is also too strong to be plausibly interpreted as (2) or (2A). Further, it is not plausibly interpreted simply as (1), partly because of its intensity and partly because of the strong expectations that the first absorption of CO_2 should lead to a bent upper state. The only plausible interpretation is as transition (1B). In view of the expectation (see Figure) that the lowest-energy

* See footnote, p. 2264

absorption should lead to a *strongly* bent upper state, the 1495-Å peak may be interpreted, in more detail, as

$$\cdots(a_2'')^2(b_2')(a_1'),\ ^1B_2 \text{ (correlating with } ^1\Delta_u) \longleftarrow \cdots(\pi_g)^4,\ ^1\Sigma_g^+ \quad . \quad (1B')$$

This leaves the interpretation of the 1390—1240-Å region to be given in more detail as

$$\cdots(a_2'')(b_2')^2(b_1''),\ ^1B_2 \text{ (correlating with } ^1\Sigma_u^+) \longleftarrow \cdots(\pi_g)^4,\ ^1\Sigma_u^+ \quad . \quad (3A')$$

raising the expectation that the upper state may be *slightly* bent. That the expectation is correct is strongly supported by the fact that in the analogous region of CS_2 (see below) there is evidence that the upper state is bent through a few degrees. In view of the remarkable dependence of apex angle upon number of occupied orbitals (irrespective of the particular nuclei concerned) we would expect the apex angle in the upper state of the ~1495-Å absorption to be less than the ground state angle of NO_2 (143° ± 11°) by a small amount which represents the effect of losing an electron from the linear-stabilizing π_g orbital. A reasonable expectation for the apex angle would be 135° ± 10°.

It is interesting that Wilkinson and Johnston find, besides the peak at *ca.* 1495 Å, three still weaker bands at 1690, 1673, and 1662 Å, which appear to represent a separate system. These bands, which are very diffuse, are also mentioned by Price and Simpson (*loc. cit.*). It is possible that they represent transition (1A).

The 3000—1760-Å absorption of N_2O is also known to subdivide into at least two regions ($\lambda_{max.}$ *ca.* 2900 and *ca.* 1900 Å), requiring different appearance pressures (see summary given by Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75).

As stated above, Mulliken (*loc. cit.*; *J. Chem. Phys.*, 1935, **3**, 720) supposes the $\bar{\sigma}_g$ to lie below the $\bar{\pi}_u$ orbital. Since if that were true we should need to draw our Figure with an "avoided crossing" and the $a_1's_A$ curve leading to $\bar{\sigma}_g$ instead of to $\bar{\pi}_u$, Mulliken's interpretation of the longest-wave-length absorption is identical with the present interpretation, provided that the upper state is formulated in the C_{2v} symbols given above. The difference is that Mulliken's interpretation implies that the $^1B_2$ upper state correlates with the $(\pi_g)^3(\bar{\sigma}_g)$, $^1\Pi_g$ linear state instead of with the $(\pi_g)^3(\bar{\pi}_u)$, $^1\Delta_u$ linear state. [In a bent molecule, the degeneracy of the $^1\Pi_g$ state would be split, leading to transitions (1A) and (1B) above.] Now, if the upper state of the first absorption correlates with $^1\Pi_g$, one might expect the analogous absorption in N_2O to be much stronger, since it should be related to the *allowed* transition

$$\cdots(\pi)^3(\bar{\sigma}),\ ^1\Pi \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The first absorption of N_2O, however, remains weak. It seems better, therefore, to regard the first absorption as related to the transition

$$\cdots(\pi)^3(\bar{\pi}),\ ^1\Delta \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is forbidden in N_2O, as is (1) in CO_2, *i.e.*, at least with N_2O, to regard $\bar{\sigma}$ as lying above $\bar{\pi}$. [Doubtless altogether the 3000—1760-Å absorption of N_2O involves absorption to the three bent upper states which correspond to $^1B_2$, $^1A_2$ (correlating with $^1\Delta_u$) and $^1A_2$ (correlating with $^1\Sigma_u^-$) of CO_2.] It is true that with COS the first absorption becomes stronger than in CO_2, but (as we explain below) this is not compelling evidence in favour of $\bar{\sigma}_g$ lying below $\bar{\pi}_u$. Further, in other molecules [*e.g.*, diatomic molecules, C_2H_2 (see Part III) and HCHO] the details of the spectra are only plausibly interpreted by supposing that the orbital analogous to $\bar{\sigma}_g$ lies above that analogous to $\bar{\pi}_u$. With no molecule does there appear to be any compelling evidence that $\bar{\sigma}_g$ (or its analogue) lies below $\bar{\pi}_u$. At least pending further evidence, therefore, we shall proceed on the assumption that $\bar{\sigma}_g$ lies above $\bar{\pi}_u$, since this implies a simpler form for our Figure. If later work should show that after all $\bar{\sigma}_g$ lies below $\bar{\pi}_u$, it would not be difficult to make the necessary changes in the present assignments.

The continuous nature of the absorption in CO_2 and N_2O does not seem surprising in view of the fact that the energy absorbed is sufficient to cause dissociation into the ground states of CO and O or N_2 and O respectively. It is clear, however, that the equilibrium form of the upper state may possess much less energy than the form reached in absorption

at $\lambda_{max.}$ from the ground state. The upper state may therefore be stable in the equilibrium form and a discrete emission spectrum may be possible. If the absorption spectrum of CO_2 at high temperatures were studied, so that transitions from high vibrational levels of the ground state were possible at sufficiently long wave-lengths, the absorption spectrum would presumably become banded.

Returning now to the 1390—1240-Å region of CO_2, we should expect from the interpretation given above that both the ν_2 bending frequency and (more strongly) the ν_1 stretching frequency of the upper state would appear in the absorption. The latter expectation follows from the fact that the $\bar{\pi}_u$ orbital is C$\leftrightarrow$O anti-bonding. For an allowed transition, only frequencies that represent vibrations which are totally symmetrical should appear strongly; if the upper state remained linear, ν_2, being then non-totally symmetrical, would not appear strongly. The bands in the region are diffuse and shaded to the red. Their separation is ~500—600 cm.$^{-1}$, but is too irregular for the structure to be interpreted in terms of a single frequency of this magnitude. Price and Simpson suggest that two progressions are present, one starting at 1380 Å and the other at 1368 Å, each with frequency intervals of *ca.* 1225 cm.$^{-1}$ and each rising to a maximum intensity at the same wave-length. However, the measured intervals of these supposed progressions vary from 1080 to 1350 cm.$^{-1}$. No doubt the difficulty of measuring the diffuse bands can partly explain this irregularity, but the variation is so great that it seems more probable that two different frequencies are involved. In this connection it should be noted that, for a reason that will be made clear in Part III, it would be possible for the bending frequency to be slightly *increased* in the upper state relative to the value of 667 cm.$^{-1}$ in the ground state (cf. N_2O below).* The stretching frequency, on the other hand, is expected to be decreased in the upper state from its value of *ca.* 1340 cm.$^{-1}$ in the ground state.

The analogue of the CO_2 1390—1240-Å system in N_2O appears to be the absorption occurring between 1520 and 1425 Å (Duncan, *J. Chem. Phys.*, 1936, **4**, 638), although the appearance pressure of this absorption is only about a tenth of that for the CO_2 system. The absorption consists of nine diffuse bands. Duncan represents their spacing by a frequency of 621 cm.$^{-1}$ in the upper state. This might represent the totally symmetrical ν_1 vibration of 1285 cm.$^{-1}$ in the ground state, though if so the drop is very great. Alternatively, 621 cm.$^{-1}$ might represent the bending vibration which has a frequency of 589 cm.$^{-1}$ in the ground state; the small increase is not implausible (see Part III). If the latter interpretation is correct, then it implies that the upper state is (slightly) bent. Sponer and Teller (*loc. cit.*, p. 109) suggest the further interpretation that two separate progressions, each with a spacing of *ca.* 1240 cm.$^{-1}$ (representing the 1285-cm.$^{-1}$ ground-state frequency), are present; but if so the drop in frequency seems surprisingly small. However, the spacing between the bands is irregular and, though this is doubtless partly due to the difficulty of measurement, it is not improbable that *two* frequencies are involved, one representing ν_2' and the other ν_1'. It is unfortunate that the diffuseness of the bands precludes resolution of the rotational fine structure to decide whether the bands are parallel or perpendicular. Whatever the correct interpretation, if ν_2' is involved the progression in it is fairly short (maximum intensity occurs at the fifth band), so that the upper state is slightly, rather than strongly, bent.

An extensive emission band system believed to be due to the CO_2 molecule is known. It appears in the carbon monoxide flame spectrum (see Gaydon and Wolfhard, *Nature*, 1949, **164**, 22). The bands lie between 5500 and 3000 Å, with maximum intensity around 4200 Å. Smyth (*Phys. Review*, 1931, **38**, 2000) was unable to find emission bands that could be ascribed to CO_2 over the range 2700—1400 Å. In other words, there appeared to be no bands corresponding to those found in absorption around 1500 Å. However, as Gaydon (*Proc. Roy. Soc.*, 1940, *A*, **176**, 505; "Spectroscopy and Combustion Theory," Chapman and Hall, London, 2nd Edn., 1948) pointed out, if the upper state is considerably bent one would expect the emission system to lie at wave-lengths much longer than those of the corresponding absorption bands. This follows from the Franck–Condon principle. The extensive range covered by the emission spectrum confirms that the molecular

* In the first absorption of CS_2, however, $\nu_3' < \nu_2''$.

dimensions change considerably in the transition. Excited CO_2 molecules in the carbon monoxide flame almost certainly arise by the reaction

$$O(^3P) + CO(^1\Sigma^+) \longrightarrow CO_2^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It follows that the excited molecules are in a triplet state (Laidler, *J. Chem. Phys.*, 1949, **17**, 221) and that this triplet state is not more than *ca.* 130 kcal./mole above the ground state. If the excited state arises from the first excited configuration, then the system is due to the transition

$$\cdots (b_2')(a_1'),\ ^3B_2 \longrightarrow \cdots (\pi_g)^4,\ ^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

i.e., involves a change of multiplicity. Gaydon assumes that the transition is to the ground state but does not point out that this must mean the transition is forbidden because of the change of multiplicity. If the ground state is not involved, the lower state must be strongly bent and (probably) triplet. Only so will it be possible for the height of the lower state above the ground state to be sufficiently low for an emission stretching to *ca.* 3000 Å to arise from an upper state produced by (6). The lower state should not be more than 30—40 kcal. above the ground state. If the ground state is not involved, then, for obvious reasons apart from one of the states' being strongly bent, the emission system does not correspond to any known absorption system; and the vibrational frequencies present are not, as Gaydon supposes, those of the ground state.

In fact, the evidence that the lower state is the ground state is unconvincing. Thus Gaydon interprets frequency differences of 2065 and 565 cm.$^{-1}$ as the 2349 cm.$^{-1}$ (ν_3) and 667 cm.$^{-1}$ (ν_2) frequencies of the ground state. The discrepancies are very large if they are due to anharmonic factors concerned in transitions to high vibrational levels of the ground state. The anharmonic factors for the lower ground-state levels are known to be very small [*e.g.*, $(x_e\omega_e)_2 = -1{\cdot}3$ cm.$^{-1}$]. The observed progressions are so long that the bands can hardly *all* be to very high levels of the ground state. In the ground state Fermi resonance occurs between the ν_2 and ν_1 levels, the resonance splitting being ~102 to 144 cm.$^{-1}$. This separation does not appear in the emission spectrum. Further, the upper state is expected to involve an excited orbital that, in comparison with the ground state, is strongly C$\longleftrightarrow$O anti-bonding. In other words, if the ground state is concerned, the transition should show progressions in ν_1 of the ground state. These progressions should be represented by pairs of bands separated by the Fermi resonance splitting and with $\sim\nu_1$ of the ground state between the pairs. The ν_1 frequency in the ground state is known to have the approximate value of 1340 cm.$^{-1}$. The anharmonicity ($x_e\omega_e$) is known to be very small (—0·3 cm.$^{-1}$), but, if the other two frequencies are markedly reduced by anharmonic factors, the ν_1'' progressions should be represented by pairs of bands separated by markedly less than 1340 cm.$^{-1}$. Now the most commonly occurring intervals in the flame spectrum (Gaydon, *loc. cit.*) are 565, 1130, and 1500 cm.$^{-1}$. Intervals that occur less frequently are 345, 925, 1355, 1700, 2065, and 2260 cm.$^{-1}$; intervals that occur still less frequently are 160, 230, 515, 780, 1865, and 1915 cm.$^{-1}$. In addition Gaydon refers to the bands' tending to occur in pairs with a separation of *ca.* 60 cm.$^{-1}$ between the members of a pair. None of these frequency differences is plausibly identified as ν_1 of the ground state. The only two that are close to the expected magnitude are 1130 and 1355 cm.$^{-1}$; but the first of these is rather low and is much more plausibly interpreted as 2×565 cm.$^{-1}$, while the second is too high. Gaydon makes no attempt to identify any of the observed frequency differences as ν_1. If the lower state is the ground state, non-appearance of progressions in ν_1 of the ground state is difficult to understand.

Let us see what interpretation of the observed frequency differences can be given if the ground state is not involved. Gaydon assumes long progressions in ν_3. However, there is no precedent in the known spectra of triatomic molecules for long progressions in the unsymmetrical stretching frequency ν_3. Further, such progressions would imply that one of the low-lying states of CO_2 has the C atom nearer to one O atom than to the other; and there is no theoretical expectation of such a lack of symmetry. In fact, if the emission involves a single upper state and a single lower state, we may confidently expect the system to be capable of interpretation in terms of four fundamental frequencies alone,

viz., ν_1', ν_2', ν_1'', and ν_2''. ν_1' and ν_1'' should both be less than 1340 cm.$^{-1}$. ν_2' and ν_2'' are likely to be less than or close to 667 cm.$^{-1}$ (the value of ν_2 in the ground state). *All* the frequency differences greater than 1340 cm.$^{-1}$ must be interpreted as overtones or combination bands of the fundamentals. 60, 160, 230, and probably 345 cm.$^{-1}$ are too small to be plausibly interpreted as fundamentals. The very commonly occurring 565-cm.$^{-1}$ frequency is an obvious choice for one of the fundamentals. It immediately enables 1130, 1700, and 2260 cm.$^{-1}$ to be interpreted as 2×565, 3×565 and 4×565 cm.$^{-1}$ respectively. Moreover, the magnitude 565 cm.$^{-1}$ makes it practically certain that this frequency is a bending one; it is too low to be plausibly chosen as a ν_1 frequency. $\nu_2'' = 565$ cm.$^{-1}$ is the obvious choice, since in an emission transition ν_2'' is likely to be more prominent than ν_2'. The existence of long progressions in ν_2'' then implies that the two states concerned differ markedly in apex angle. Since we have argued that the lower state must be strongly bent, the upper must therefore be linear or only slightly bent. This is in contrast to Gaydon's interpretation that the transition is from a strongly bent upper to a linear lower (ground) state. Since the emission takes place from a hot source (~600° C in the " glow " of oxidizing carbon monoxide and a much higher temperature in the ordinary flame of carbon monoxide), we expect ν_2' also to appear in the system, but probably less prominently than ν_2''. $\nu_2' = 515$ cm.$^{-1}$ is the obvious choice to try. Such a choice may at once explain the tendency of bands to occur in pairs with *ca.* 60 cm.$^{-1}$ between the members of a pair since 565—515 is close to 60. On account of Boltzman factors, we should not expect the frequency 2×515 cm.$^{-1}$ to be prominent; and, in agreement, no frequency of *ca.* 1030 cm.$^{-1}$ appears. The only likely choices for the ν_1 frequencies (since they must be less than *ca.* 1340 and since 1130 cm.$^{-1}$ has already been identified) are 925 and 780 cm.$^{-1}$. Of these, it is 925 cm.$^{-1}$ which, being the commoner of the two, is likely to represent ν_1''. Such a choice probably accounts also for (*a*) *ca.* 1865 cm.$^{-1}$, since $2 \times 925 = 1850$, (*b*) *ca.* 345 cm.$^{-1}$, since $925 - 565 = 360$, (*c*) *ca.* 1500 cm.$^{-1}$, since $925 + 565 = 1490$, and (*d*) *ca.* 2065 cm.$^{-1}$, since $925 + (2 \times 565) = 2055$. The commonness of occurence of, *e.g.*, 1500 cm.$^{-1}$ is understandable, since it is composed from a very commonly and a fairly commonly occurring interval. This leaves $\nu_1' = 780$ cm.$^{-1}$. Just as 2×515 cm.$^{-1}$ did not occur, so we should not expect 2×780 cm.$^{-1}$ to appear; nor is it found. The choice, however, plausibly identifies (*a*) *ca.* 1355 cm.$^{-1}$, since $780 + 565 = 1345$, (*b*) *ca.* 1915 cm.$^{-1}$, since $780 + (2 \times 565) = 1910$, (*c*) *ca.* 160 cm.$^{-1}$, since $925 - 780 = 145$, and (*d*) *ca.* 230 cm.$^{-1}$, since $780 - 565 = 215$. This accounts for all the observed frequency intervals and moreover the whole forms an entirely reasonable, consistent, interpretation. The magnitudes of $2\nu_2''$ and $2\nu_2'$ are such that no Fermi resonance is expected with the ν_1 frequencies; and in agreement no further spearation remains to be accounted for by such resonance. Moreover, it is very reasonable that ν_2'' should be less than ν_2', and ν_1'' less than ν_1'; for the lower, strongly bent state (*a*) is likely, for a reason that will be referred to again in Part III, to have more resistance to bending than the upper linear or nearly linear state and (*b*) almost certainly involves the $a_1's_A$–$\bar{\pi}_u$ orbital which tends to lose its C$\leftrightarrow$O anti-bonding character as the molecule bends.

Summarizing, $\nu_2'' = 565$, $\nu_1'' = 925$, $\nu_2' = 515$, $\nu_1' = 780$ cm.$^{-1}$ and it is clear that the ground state is not involved and that the system consists of a single electronic transition. All the vibrations concerned are totally symmetrical with respect to the bent molecule and therefore there is no symmetry restriction on the number of quanta of each that may occur. The O(^{3}P) atom in (6) is expected to approach the C atom of the CO molecule along the C–O line, in such a way that an unpaired $p\sigma$ electron of the O atom interacts with a σ lone pair on the C atom. It appears probable therefore that the resulting state of CO_2 is $^3\Pi$. Having regard to what are the low-lying states (see the Figure), this must be $^3\Pi_g$. Our analysis of the flame bands requires this state to be linear or nearly linear; it is satisfactory that our Figure (though not Mulliken's correlation diagram) predicts linearity for the $^3\Pi_g$ state. The lowest excited state of CO_2, according to the Figure, should be the strongly bent $^3B_2$ (or less probably $^3A_2$) state. The flame bands are therefore most probably to be identified as due to the allowed transition

$$^3\Pi_g \longrightarrow {}^3B_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Further, there is a very low probability that a triplet, strongly bent (apex angle $135° \pm 10°$), excited state of CO_2 would emit radiation and pass to the ground state. It would behave almost like a separate chemical species, a fact that may have something to do with the " latent energy " that has been reported for carbon monoxide flames (David, Leah, and Pugh, *Phil. Mag.*, 1941, **31**, 156).

(ii) CO_2^+. Discharges through CO_2 give rise to a pair of strong bands at 2882 and 2896 Å. It is known (Bueso-Sanllehí, *Phys. Review*, 1941, **60**, 556) that these are due to the CO_2^+ molecule; that they represent the transition $\cdots(\sigma_u)(\pi_u)^4(\pi_g)^4$, $^2\Sigma_u^+ \longrightarrow \cdots(\sigma_u)^2(\pi_u)^4(\pi_g)^3$, $^2\Pi_g$; that (as would be expected from the present considerations) the molecule is linear in both upper and lower states; and that the transition causes little change of the molecular dimensions.

The negative glow of discharges through streaming CO_2 or excitation of CO_2 by electron impact gives rise to an extensive system of weaker bands lying between 5000 and 2900 Å. The bands were first observed by Fox, Duffendack, and Barker and have been studied by Smyth, by Schmid, and especially by Mrozowski (*Phys. Review*, 1941, **60**, 730; 1942, **62**, 270; *Rev. Mod. Phys.*, 1942, **14**, 216). According to Pearse and Gaydon (" The Identification of Molecular Spectra," Chapman and Hall, London, 2nd Edn., 1950) these bands are believed to be due to the neutral CO_2 molecule, but this neglects the work of Mrozowski which appears to show conclusively that the bands are due to CO_2^+ and that they represent the transition $\cdots(\pi_u)^3(\pi_g)^4$, $^2\Pi_u \longrightarrow \cdots(\pi_u)^4(\pi_g)^3$, $^2\Pi_g$. As would be expected from the present arguments, rotational analysis shows that the molecule is linear in both upper and lower states. In accord with this, only ν_1 vibrations appear strongly. The degradation of the bands to the red and the extensive range covered by the spectrum are understandable in view of the properties of the π_u and π_g orbitals.

(iii) CS_2. From our Figure we should expect the first absorption of the CS_2 molecule to be due to transition to a configuration correlated to $(\pi_g)^3(\pi_u)$. The first absorption consists of a large number of bands between 3980 and 2767 Å ($\lambda_{max.}$ ~3200 Å) (Wilson, *Astrophys. J.*, 1929, **69**, 34). It is weak, requiring several cm. pressure with a 1-m. absorption path, and is, like the first absorption peak of CO_2, plausibly interpreted as (1B′). That the CS_2 spectrum, unlike that of CO_2, consists of discrete bands is understandable since the excitation energy for CS_2 lies below that required for dissociation. One would expect the upper state to be considerably bent and to possess a considerably increased C–S distance over the ground state. Mulliken (*J. Chem. Phys.*, 1935, **3**, 720) early concluded that the upper state of the system was bent in its equilibrium form. Liebermann (*Phys. Review*, 1941, **60**, 496), from a partial vibrational analysis, showed that long progressions in ν_2' occur and also that the intensity of bands originating from $v_2'' = 2$, relative to bands originating from $v_2'' = 0$ but proceeding to the same upper level, is considerably greater than would be expected from the Boltzmann factor alone. Both these facts strongly suggest a considerably bent upper state. In addition, one-quantum jumps of ν_2' occur, which would be expected for a bent upper state but not for a linear one. Rotational analysis of six of the bands (at 3673, 3637, 3601, 3535, 3501, and 3468 Å) by Liebermann (*ibid.*, 1940, **58**, 183; 1941, **59**, 106A; 1941, **60**, 496) has shown them to be of the parallel type with simple P and R branches, closely resembling $^1\Sigma_u^+ \longleftarrow {}^1\Sigma_g^+$ bands of a molecule in which both states were linear. If, however, the upper state *were* linear, alternate bands of the ν_2' progression should be of a $\Pi \longleftarrow \Sigma$ type, which they are not. In fact, Liebermann has shown that the observed simple rotational structure is equally compatible with any apex angle between 125° and 180°. (As estimated above for the first excited state of CO_2, $135° \pm 10°$ would be a reasonable value for the apex angle in the excited state.) If the upper state is bent, the parallel nature of the bands identifies them as $^1B_2 \longleftarrow {}^1\Sigma_g^+$, in agreement with the expected interpretation (1B′). Mulliken (*ibid.*, 1941, **60**, 506) has earlier shown how the observed characteristics are compatible with interpretation (1B′). The only difference between his and the present interpretation is that he supposed the upper state correlated with $^1\Pi_g$ rather than with $^1\Delta_u$. The rotational structure, on the assumption of a markedly bent molecule, indicates a considerable increase of C–S length on excitation. This is as expected for transition (1B′) and implies that progressions in ν_1' should be present. These have not yet been identified. It may be

noted that ν_1', when found, is expected to be somewhat greater than its value (410 cm.$^{-1}$) in the $^1\Sigma_u^+$ state (see below) since the $a_1's_A$–π_u orbital is expected to lose some of its antibonding character as the molecule bends; on the other hand, ν_1' should be less than ν_1'' which is 657 cm.$^{-1}$. The magnitude of the angular restoring forces is considerably reduced by the excitation, the frequency ν_2 being 275 cm.$^{-1}$ in the upper state as against 401 cm.$^{-1}$ in the ground state. Transition (1A) has not yet been identified, but may be present in the 3980—2767-Å system.

The second absorption system of CS_2 consists of a much more intense set of bands with $\lambda_{max.}$ *ca.* 1970 Å. Almost certainly this system corresponds to the CO_2 system of $\lambda_{max.}$ *ca.* 1335 Å (Price and Simpson, 1939, *loc. cit.*) and may be interpreted as (3A'). Mulliken has previously briefly suggested that the absorption represents (3). According to the present considerations, the upper state would be expected to be slightly bent, while the C–S length would be expected to be considerably increased relatively to the ground state. That the transition covers an extensive range of the spectrum (2300—1800 Å) is not therefore surprising. Price and Simpson have already concluded that the upper state is bent through a few degrees. As a result the molecule acquires one low moment of inertia and this explains the many heads, separated by about 40 cm.$^{-1}$, observed in each band under high dispersion. The bands as a whole are shaded to the red, as expected. Only one upper-state vibration appears as a long progression. This has a frequency of *ca.* 410 cm.$^{-1}$ (390—430 cm.$^{-1}$), and undoubtedly represents the symmetrical valency-stretching frequency ν_1 which is 657 cm.$^{-1}$ in the ground state.

(iv) COS. The first absorption of COS (2550—1600 Å) is much stronger than that of CO_2 or CS_2. This might be taken as evidence that the first absorption of CO_2 or CS_2 is to an upper state that correlates with $^1\Pi_g$ rather than with $^1\Delta_u$, *i.e.*, that $\bar{\sigma}_g$ lies below $\bar{\pi}_u$. The corresponding absorption of COS might then be expected to be much stronger because of the absence of a centre of symmetry in linear COS; the transition $^1\pi \leftarrow\!\!- {}^1\Sigma^+$ is allowed, whereas $^1\Pi_g \leftarrow\!\!- {}^1\Sigma_g^+$ is forbidden. An alternative explanation is equally valid, however, *viz.*, that, though the transitions $^1A_2 \leftarrow\!\!- {}^1\Sigma_g^+$ are symmetry-forbidden for CO_2 and CS_2, the analogous transitions $^1A'' \leftarrow\!\!- {}^1\Sigma^+$ are allowed for COS (apart from the Franck–Condon restriction on intensity). There should be two of these $^1A'' \leftarrow\!\!- {}^1\Sigma^+$ transitions, corresponding to the $^1A_2$ upper states of CO_2 or CS_2 correlating with $^1\Delta$ and $^1\Sigma_u^-$. In addition there should be a third transition, to a bent upper state, corresponding to the $^1B_2$ state of CO_2 or CS_2 correlating with $^1\Delta_u$. It is significant that at very low pressures (~0·01 mm. in a 1-m. path length) the absorption sub-divides into several wide diffuse bands (2380—2150, 2120—2080, and 2050—1860 Å) apparently involving three separate electronic transitions (Price and Simpson, 1939, *loc. cit.*). [That the first absorption of N_2O remains weak, while that of COS becomes comparatively strong, may be because the electronegativities of N and O are closer than those of S and O (Walsh, *Proc. Roy. Soc.*, 1951, *A*, **207**, 13), so that a bent state of NNO is not so far removed from C_{2v} symmetry as a bent state of COS.]

The second absorption region consists of some seven diffuse bands extending from *ca.* 1550 to *ca.* 1410 Å with $\lambda_{max.}$ at 1510 Å (Price and Simpson, 1939, *loc. cit.*). It undoubtedly corresponds to the CO_2 absorption of $\lambda_{max.}$ 1335 Å and the CS_2 absorption of $\lambda_{max.}$ 1970 Å. A progression probably involving ν_1' is present with a difference of *ca.* 760 cm.$^{-1}$. The corresponding frequency in the ground state is 859 cm.$^{-1}$. Price and Simpson refer to the 1510-Å system as a possible first member of a Rydberg series, but this would not accord with the present interpretation as an intra-valency-shell transition and as corresponding to the CO_2 and the CS_2 system discussed above.

(v) $HgCl_2$, $HgBr_2$, HgI_2. According to analyses by Wehrli (*Helv. Phys. Acta*, 1938, 339; 1940, **13**, 153) and Sponer and Teller (*J. Chem. Phys.*, 1939, **7**, 382; *Rev. Mod. Phys.*, 1941, **13**, p. 106), the upper states of the 1731—1670, 1862—1813, and 2108—2066 Å absorption regions of $HgCl_2$, $HgBr_2$, and HgI_2 respectively are probably $^1\Sigma_u^+$. The absorption regions are therefore to be interpreted as (3). As expected, the bands are degraded to the red; and the stretching frequencies in the upper states are considerably reduced relative to the ground state. The excited states do not depart appreciably from linearity. This of course is quite possible according to the present arguments. Although the b_1''–$\bar{\pi}_u$ curve falls from right to left in the Figure its curvature is not necessarily

sufficient to cause the $^1\Sigma_u^+$ states to be bent. Indeed, since the b_1''–$\bar{\pi}_u$ curve falls from right to left because the orbital is bonding between the end atoms, it is not unlikely that the curvature would be less when the central atom is very large (as Hg) and the end atoms are therefore far apart, whatever the molecular shape. It is significant that ν_2' does occur in the spectra though, in accord with the selection rules for a strictly linear upper state, always as two quanta; its occurrence indicates that the forces controlling bending have changed as a result of the transition. ν_3' does not occur in the spectra. ν_2' is less than ν_2'' by a few cm.$^{-1}$ for each molecule (65, 36, and 30 cm.$^{-1}$, compared with 70, 41, and 33 cm.$^{-1}$ for $HgCl_2$, $HgBr_2$, HgI_2 respectively). In accord with the above absorption representing transitions to $^1\Sigma_u^+$ upper states a longer-wave-length absorption continuum has been observed for each molecule (Wieland, *Z. Physik*, 1932, **76**, 801; **77**, 157). The maxima of these continua are at *ca.* 1810 Å ($HgCl_2$), *ca.* 1950 Å ($HgBr_2$), and *ca.* 2660 Å (HgI_2). The continua should represent transitions to strongly bent $^1B_2$ upper states, correlating with $^1\Delta_u$.

(vi) NO_2. That a Rydberg series exists in the spectrum of NO_2 (Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106), the members of which are accompanied by very little vibrational structure, implies that a state of NO_2^+ exists which is non-linear and has an angle not very different from that in the ground state of NO_2. As Price and Simpson have already remarked, the Rydberg series can hardly proceed to the ground state of NO_2^+ since there is strong evidence that the latter is linear and the Franck–Condon principle would forbid photo-ionization to such a state without a large amount of accompanying vibration. The magnitude of the ionization limit obtained from the Rydberg series (12·3 v) makes it very probable that the series leads to the *first* excited state of NO_2^+ (certainly to a very low-lying excited state). We have, therefore, evidence that the first (or at least a very low-lying) excited state of NO_2^+ is considerably bent, as the present arguments would lead one to expect.

(vii) NO_2. From our Figure, for a ground-state angle of 143° ± 11°, the allowed transitions of longest wave-length for NO_2 should be

$$\cdots(a_2'')^2(b_2')^2(b_1''),\ ^2B_1 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad . \quad (10)$$

$$\cdots(a_2'')^2(b_2')^2(\bar{a}_1'),\ ^2A_1 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad . \quad (11)$$

$$\cdots(a_2'')^2(b_2')(a_1')^2,\ ^2B_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad . \quad (12)$$

Transitions of the types

$$\cdots(a_2'')(b_2')^2(a_1')^2,\ ^2A_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad . \quad (13)$$

$$\cdots(a_2'')^2(b_2')(a_1')(b_1''),\ ^2A_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad . \quad (14)$$

would be forbidden. By Mulliken's reasoning (*Rev. Mod. Phys.*, 1942, **14**, 204), the observed absorption bands of NO_2 between 9000 and 3200 Å (strongest between 5750 and 3520 Å) may be attributed to one or more of the transitions (10), (11), and (12). Pearse and Gaydon (*loc. cit.*) comment that more than one electronic system may be involved in the bands. Expressions (10), (11), and (12) supply examples of transitions that might be polarized in any of the three possible axes, might lead to an increase or a decrease of apex angle, and might markedly increase or hardly change the N–O distance. Transitions that cause a marked change of angle or N–O distance would be expected to occupy an extensive region of the spectrum.

Towards shorter wave-lengths should come the transitions

$$\cdots(a_2'')^2(b_2')(a_1')(\bar{a}_1'),\ ^2B_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad (15)$$

and

$$\cdots(a_2'')(b_2')^2(a_1')(b_1''),\ ^2B_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad . \quad (16)$$

followed at still shorter wave-lengths by

$$\cdots(b_2')(a_2'')^2(b_2')^2(a_1')^2,\ ^2B_2 \longleftarrow \cdots(b_2')^2(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad (17)$$

Both these are allowed and they are of the same symmetry type.

NO_2 has a second absorption system between 2600 and 2270 Å. Certain of the observed bands of this system are known to be of the parallel type with red-degraded

K-structure (Mulliken, 1942, *loc. cit.*), *i.e.*, polarized parallel to the axis of least moment of inertia and so to the O···O line, NO_2 being an approximately symmetric top molecule. This implies that the bands are part of a $B_2 \leftarrow\!\!- A_1$ system, the transition being assumed to be electronically allowed. Mulliken chooses either (15) or (16) to represent the system. (17) might be considered as another possibility, but, whereas (15) should lead to a small *increase* of apex angle and (16) to only a small decrease, (17) should cause a very marked decrease. Rotational analysis of the 2491-Å band has yielded angles in the ground and the excited state (154° ± 4° and 154° ± 6° respectively) which differ little (Harris and King, *J. Chem. Phys.*, 1940, **8**, 775). This favours assignment to (15) or (16) rather than to (17). However, some doubt must attach to the conclusions from the rotational analysis since (*a*) the ground state angle obtained is very different from the angle reported from electron-diffraction studies (132°), and (*b*) it is not based on a complete resolution of the *J*-structure. That the angle has in fact changed from the ground state to the upper state is indicated by the appearance in the spectrum of vibrational bands probably representing the upper-state bending frequency ν_2 (Harris, King, Benedict, and Pearse, *ibid.*, p. 765). The frequency is 523 cm.$^{-1}$, compared with 648 cm.$^{-1}$ in the ground state. Expressions (15) and (16) should lead to a considerable increase of N–O distance. In agreement, from the rotational analysis of the band at 2491 Å, it has been concluded that this distance is 1·41 ± 0·06 Å in the upper state, compared with 1·28 ± 0·03 Å in the ground state. One would expect the totally symmetrical stretching vibration (probably 1320 or 1373 cm.$^{-1}$ in the ground state) to appear in the upper state. A frequency of 714 cm.$^{-1}$ possibly represents this. However, the vibrational analysis of the system is as yet far from satisfactory, one difficulty being that the separations to long wave-lengths of the apparent origin of the system do not obviously correspond to the frequencies found in the infra-red spectrum. (In order to avoid absorption by N_2O_4, the spectrum has been studied at temperatures above 100° C, so that a number of bands due to transitions from vibrational levels of the ground state appear.) The difficulty is enhanced by the fact that the Raman spectrum of NO_2 has not yet been observed (owing to the molecules absorbing throughout the visible and the near ultra-violet regions) with the result that the ν_1'' frequency is not definitely known. It should also be noted that predissociation of the bands of shorter wave-length shows that a second electronic upper state is concerned in the absorption.

A further absorption system of NO_2 occurs between 1600 and 1350 Å with $\lambda_{max.}$ at 1467 Å (Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106). This contains a very long vibrational progression, covering at least some fifty bands. The frequency difference is 200 cm.$^{-1}$ and almost certainly represents the $\nu_2 a_1$ deformation vibration. It follows that the equilibrium form of the upper state has an apex angle very different from that of the ground state, and also has considerably reduced angular restoring forces. This suggests that the upper orbital concerned is a_1'–$\bar{\pi}_u$, whose curve rises so steeply in the Figure, and perhaps that the lower orbital is one of the bonding orbitals. In other words, it is very plausible to assign transition (17) to the system. The bands of the system should be of the parallel type, but a decision awaits study under higher dispersion.

According to the Figure, the following transition should lie very close to (17):

$$\cdots(a_1')(b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ {}^2A_1 \leftarrow\!\!- \cdots(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1'),\ {}^2A_1 \quad (18)$$

It too should lead to a considerable decrease of apex angle, though not quite as much as (17). It should also lead to an increase of N–O distance. It is an allowed transition that should be *z*-polarized. Price and Simpson (*loc. cit.*) find a second absorption system to be present in the 1600—1350-Å region. It too shows a long vibrational progression, the frequency difference being roughly the same as for the system identified as (17). It seems very plausible that this represents transition (18). When the 1600—1350-Å system is examined under high dispersion, it should be possible to test whether the bands ascribed to (18) are in fact of the expected perpendicular type.

A further transition,

$$\cdots(b_1'')(a_1')^2(b_2')^2(a_2'')^2(b_2')(a_1')^2,\ {}^2B_1 \leftarrow\!\!- \cdots(b_1'')^2(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1'),\ {}^2A_1 \quad (19)$$

should lie at slightly shorter wave-lengths than (17) and (18). Transition (19) is allowed, and x-polarized, and should lead to an increase of N–O distance and a small decrease of apex angle. According to Price and Simpson's photograph (*loc. cit.*), there are faint narrow bands in the 1350—1300-Å region (which may be a continuation of the 1600—1350-Å system) followed by a strong progression beginning at 1280 Å and undoubtedly representing one of the Rydberg transitions of the molecule. Just on the long-wave-length side of the latter occur weaker, diffuse bands which Price and Simpson ascribe to transitions from vibrating ground states. This seems unlikely in view of the Boltzmann factors involved. More plausibly, the bands either represent (19) or form part of the Rydberg transition, all being due to excitation from the vibrationless ground state and the (O, O) band not being the strongest member of the system.

The absorption in the 1600—1350-Å region is strong, requiring an appearance pressure hardly greater than that required to bring out the Rydberg bands at shorter wave-lengths. In part this can be attributed to the presence of two (and perhaps three) transitions all occurring in the same region. Further, a transition such as (17) can be regarded as belonging to the $V \longleftarrow N$ class. It is related to a $\sigma_g \longleftarrow \sigma_u$ transition, wherein there is no change of angle and the wave function of the upper orbital is of the same type as that of the lower except for the possession of an extra node along the chain of atoms. Both (17) and (18) have the characteristic of $V \longleftarrow N$ transitions in that an electron is partially transferred from the end atoms to the central atom. However, a fuller discussion of why transitions (17) and (18) should have high intensity (as well as an examination of the bands under high dispersion) is required before the assignments can be considered really satisfactory. Until this is done, the assignments must be regarded as tentative, though plausible.

Price and Simpson attribute the absorption to excitation of a "π" electron in the NO bonds. According to the present assignments, however, the absorption primarily involves only orbitals which are symmetrical with respect to reflection in the molecular plane.

(viii) SO_2. In the ground state of SO_2 the only low-lying vacant orbital (see the Figure) should be the uppermost b_1''. Next in order but considerably above b_1'' comes $\bar{a}_1'$. Remembering that the apex angle in the ground state is 119°, we see that the transitions of longest wave-length should fall into two groups. The first should sub-divide as follows:

$$\cdots (a_2'')^2(b_2')^2(a_1')(b_1''),\ {}^1B_1 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2,\ {}^1A_1 \quad . \quad . \quad (20)$$

This is an allowed transition that should give rise to perpendicular bands (the molecule being assumed to be an approximately symmetric top in both lower and upper states). Further, it should lead to a small increase of apex angle and probably to a small increase of S–O length:

$$\cdots (a_2'')(b_2')^2(a_1')^2(b_1''),\ {}^1B_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2,\ {}^1A_1 \quad . \quad . \quad (21)$$

This is an allowed transition that should give rise to parallel bands and lead to a moderate decrease of apex angle and increase of S–O length.

$$\cdots (a_2'')^2(b_2')(a_1')^2(b_1''),\ {}^1A_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2,\ {}^1A_1 \quad . \quad . \quad (22)$$

This is a forbidden transition.

Experimentally, SO_2 is known to have absorption bands stretching from *ca.* 3900 to 2600 Å. Metropolis and Beutler (*Phys. Review*, 1940, **58**, 1078) showed that the regions from *ca.* 3900 to 3400 Å ($\lambda_{max.}$ *ca.* 3740 Å) and from *ca.* 3400 to 2600 Å ($\lambda_{max.}$ 2940 Å) belonged to separate transitions. The origin of the former is at 25,775 cm.$^{-1}$ (3880 Å). The latter region is the stronger, having a maximum molecular extinction coefficient of ~400 (Garrett, *J.*, 1915, 1324). The characteristics of the bands in the 3900—3400-Å region are as follows. They possess a J-structure degraded towards the red and a K-structure degraded towards the violet, the latter diverging more slowly than the former. Metropolis (*ibid.*, 1941, **60**, 283) has shown that this implies a small increase both of apex angle and of S–O length in the excited state. The conclusion is confirmed by the

vibrational structure of the transition, especially by the absence of long progressions involving the deformation frequency. That the changes are small is also confirmed by the fact that the strongest band is that representing a combination of only one quantum of each of the totally symmetrical vibrations. The arrangement of the K sub-bands shows that the transition is probably of the perpendicular type. The 3900—3400-Å system thus agrees very well with the expected characteristics of transition (20). Mulliken has previously assigned (20) to the region.

From a vibrational analysis of the 3400—2600-Å region, Metropolis (*ibid.*, p. 295) showed that (1) the origin lay at 29,622 cm.$^{-1}$ (3376 Å), the transition thus covering a very extensive region, (2) both apex angle and bond distance change markedly in the transition, (3) the frequencies in the upper state are 794 (symmetrical stretching), 345 (symmetrical deformation), and 833 cm.$^{-1}$ (anti-symmetrical stretching), compared with 1152, 525, and 1361 cm.$^{-1}$ respectively in the ground state, (4) from the vibronic selection rules, because both a_1 and b_2 vibrations appear in the upper state, the electronic part of the latter is either $^1A_1$ or $^1B_2$, and (5) the values for the excited-state frequencies when substituted in theoretical formulæ for a valence force model yield an apex angle of probably *ca.* 100° compared with 120° in the ground state, *i.e.*, they show that the apex angle decreases in the transition. Metropolis also noted that the rotational structure showed none of the regularity present in, *e.g.*, the 3900—3400-Å bands. This implies that the dimensions of the molecule have so changed that the upper state is not, even approximately, a symmetric top. This in turn makes rotational analysis difficult, but at least makes it practically certain that the angle must have decreased and the length increased during the excitation. The characteristics of the 3400—2600-Å bands thus agree very well with identification of the transition as (21). Mulliken has previously assigned (21) to the system.

The second group of transitions expected from the Figure is as follows:

$$\cdots (b_2')(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1A_2 \longleftarrow \cdots (b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (23)$$

This is a forbidden transition.

$$\cdots (a_1')(b_2')^2(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1B_1 \longleftarrow \cdots (a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (24)$$

This is an allowed transition which should lead to a moderate decrease of apex angle and a moderate increase of S–O distance. It should give rise to perpendicular bands.

$$\cdots (b_1'')(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1A_1 \longleftarrow \cdots (b_1'')^2(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (25)$$

This is also an allowed transition which should give rise to bands of the perpendicular type. It should cause a greater increase of S–O distance than transition (24) [because the (a_1') orbital is less S$\longleftrightarrow$O bonding than the (b_1'')], but comparatively little change in apex angle.

The following two allowed transitions may lie fairly close to the second group above:

$$\cdots (b_2')^2(a_1')(a_1'),\ ^1A_1 \longleftarrow \cdots (b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (26)$$

$$\cdots (b_2')(a_1')^2(\bar{a}_1'),\ ^1B_2 \longleftarrow \cdots (b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (27)$$

Transition (26) would be perpendicular, and (27) parallel. The former should cause a very marked, and the latter a small increase of apex angle.

Experimentally, SO_2 shows a region of absorption from *ca.* 2400 to 1800 Å ($\lambda_{max.}$ *ca.* 2000 Å). Its maximum molecule extinction coefficient is several times that of the 3400—2600-Å system. Duchesne and Rosen (*J. Chem. Phys.*, 1947, **15**, 631) have shown, by vibrational analysis, that at least two and probably three electronic transitions are involved in the region.* The first of these has its origin at 42,170 cm.$^{-1}$ (2371 Å), the vibrational frequencies appearing in the upper state being 963 (symmetrical stretching)

* The possible third transition is to an upper state having vibrational frequencies of 845 (symmetrical stretching) and 360 cm.$^{-1}$ (symmetrical bending). Rosen (*J. Phys. Radium*, 1948, **9**, 155) gives its origin as 45,499 cm.$^{-1}$ (2198 Å) and mentions the existence of a fourth transition whose origin is at 47,510 cm.$^{-1}$ (2105 Å) with upper-state frequencies of ~800 (ν_1) and 350 cm.$^{-1}$ (ν_3).

and 379 cm.$^{-1}$ (symmetrical bending). The high intensity and the absence of anti-symmetrical vibrations show that the transition is an allowed one. The partially resolved rotational structure of the bands of this system shows that they are of the perpendicular type, the *K*-structure being degraded towards the red. The *J*-structure remains almost completely unresolved, but seems also to be degraded towards the red. Duchesne and Rosen conclude that the transition causes a fairly marked decrease in apex angle and a small increase in bond length. These conclusions are the more reasonable when the upper-state frequencies are compared with those obtained by Metropolis for the 3400—2600-Å system. In agreement with the small increase in bond length, transitions with many quanta of the symmetrical stretching frequency are not strong. These conclusions are not as definite as one could wish, but are in fair agreement with the characteristics expected for transition (24). Mulliken has assigned (26) and (27) to the *ca.* 2000-Å region, but both these should cause a considerable increase of apex angle; in addition, (27) would be of the parallel type.

The second electronic transition involved in the 2400—1800-Å system has its origin at 44,236 cm.$^{-1}$ (2260 Å) and is stronger than the first. The vibrational frequencies appearing in the upper state are 775 (ν_1) and 375 cm.$^{-1}$ (ν_2). The intensity and the absence of anti-symmetrical vibrations make it virtually certain that the transition is electronically allowed. No rotational analysis has yet been made, except to show that the structure is not identical with that of the first transition in the region. However, the magnitude of the symmetrical stretching frequency suggests that the bond length has increased more in the second electronic transition than in the first. This conclusion is supported by the appearance of strong bands representing many quanta of the symmetrical stretching frequency. The rather scanty known characteristics of the transition are therefore not incompatible with its assignment to (25).

If the possible third and fourth transitions in the 2400—1800-Å region should be confirmed, the expectation is that they will be found to represent (26) and (27).

(ix) SeO_2. Selenium dioxide possesses the following absorption regions :

(*a*) 5000—3400 Å ($\lambda_{max.} \sim 4080$ Å) (Duchesne and Rosen, 1947, *loc. cit.*). The origin appears to be at ~4570 Å. Prominent progressions involving the symmetrical bending frequency of the upper state (~200 cm.$^{-1}$) are present. Progressions involving the symmetrical stretching frequency are not prominent. It follows that whereas the apex angle changes appreciably in the transition, the Se–O bond length changes little. The absorption is fairly strong. This and the complete absence of anti-symmetrical vibrations show the transition to be allowed.

Duchesne and Rosen (*Nature*, 1946, **157**, 692) at first suggested that the absorption region might be analogous to that of SO_2 between 3900 and 3400 Å. Later, because this SO_2 absorption causes a more marked change of length than of angle, while the SeO_2 absorption causes a change of angle more marked than that of bond length, they abandoned this suggestion in favour of one whereby the SeO_2 transition was analogous to the SO_2 transition of origin at 2371 Å. The latter suggestion seems the more probable also because the former entails that the next absorption system of SeO_2 (3300—2300 Å) would be analogous to the SO_2 3400—2600-Å system and therefore show little or none of the expected long-wave-length shift. This implies that two electronic absorption systems of SeO_2 should be found in the infra-red region, and that the 5000—3400-Å region may be tentatively interpreted as (24).

(*b*) 3300—2300 Å ($\lambda_{max.} \sim 2700$ Å) (Duchesne and Rosen, *Physica*, 1941, **8**, 540). The origin is at 3000 Å. The most prominent feature or this absorption is the presence of progressions involving the symmetrical stretching vibration (*ca.* 665 cm.$^{-1}$ in the upper state compared with 900 or 910 cm.$^{-1}$ in the ground state). It therefore appears that the transition causes a marked change of bond length but little change of apex angle. It is probably analogous to the SO_2 system of origin at 2260 Å, and may be tentatively identified as (25).

(x) TeO_2. Tellurium dioxide possesses an absorption region from 4500 and 3000 Å with $\lambda_{max.}$ near 3550 Å (Duchesne and Rosen, 1947, *loc. cit.*). The only upper-state frequency that appears strongly is one of 650 cm.$^{-1}$, representing the symmetrical

stretching frequency (815 cm.$^{-1}$ in the ground state). This indicates that whereas the length has increased considerably during the excitation, the apex angle has changed comparatively little. There is little doubt that the system corresponds to that at 3300—2300-Å for SeO_2. It may be interpreted as (25). There should be several systems of longer wave-length to be found.

(xi) O_3. Ozone is an 18-electron molecule and has a ground-state apex angle not greatly different from that of SO_2. Its spectroscopic transitions should therefore correspond to those of SO_2. It has a weak absorption system in the visible region (7585—4380 Å; $\varepsilon_{max.} = 1{\cdot}12$), centred particularly on two strong, diffuse bands in the orange at about 5730 and 6020 Å (Colange, *J. Phys. Radium*, 1927, **8**, 254; Wulf, *Proc. Nat. Acad. Sci.*, 1930, **16**, 507). There are also very weak absorption bands in the infra-red (Wulf, *loc. cit.*). We suggest that one of these weak absorption regions represents transition (20), and that they therefore correspond to the SO_2 absorption of $\lambda_{max.}$ *ca.* 3740 Å. Ozone has a fairly strong absorption system in the region 2900—2300 Å ($\lambda_{max.}$ 2550 Å; $\varepsilon_{max.} \sim 2800$), which has about the same maximum extinction coefficient as the 2400—1800-Å system ($\lambda_{max.}$ *ca.* 2000 Å) of SO_2 (Wulf and Melvin, *Phys. Review*, 1931, **38**, 330). We suggest, therefore, that the 2900—2300-Å system is to be interpreted as involving some of the transitions (24) to (27). Transition (21) may give rise to known weaker absorption bands of O_3 between 3525 Å and the long-wave-length end of the 2900—2300-Å system (Fowler and Strutt, *Proc. Roy. Soc.*, 1917, *A*, **93**, 577; Wulf and Melvin, *loc. cit.*; Jakowlewa and Kondratjew, *Physikal. Z. Sowjetunion*, 1932, **1**, 471). If so, these absorption bands correspond to the 3300—2600-Å system for SO_2 ($\lambda_{max.}$ 2940 Å). The bands are diffuse and tend to degrade to the red, as expected for bands belonging to transition (21), but with no rotational structure resolved. Upper-state vibrational frequencies of ~300 and ~600 cm.$^{-1}$ appear. The former is probably ν_2 (705 cm.$^{-1}$ in the ground state), and the latter probably ν_1 (1110 cm.$^{-1}$ in the ground state). If these tentative interpretations are accepted, each transition in O_3 is shifted to long wave-lengths of its analogue in SO_2. This appears resonable, at least for those transitions [(21), (24), (25) and (27)] that involve transfer of an electron from the end atoms to the central atom.

Ozone emission bands have been observed between 4465 and 3090 Å in a mild condensed discharge through oxygen (Johnson, *Proc. Roy. Soc.*, 1924, *A*, **105**, 683). It is probable that these represent the reverse of one of the transitions involved in the 2900—2300-Å system. Transitions involving a considerable decrease in apex angle in the equilibrium form of the upper state could appear in emission (see the Figure) well to the long-wave-length side of the corresponding absorption bands.

(xii) NOCl. Nitrosyl chloride is a further 18-electron molecule, whose transitions should therefore correspond to those of SO_2 and O_3. It possesses two systems of weak absorption in the visible region (Goodeve and Katz, *Proc. Roy. Soc.*, 1939, *A*, **172**, 432). The shorter-wave-length system (maximum at 4750 Å) shows little structure. The longer-wave-length system (maximum at 6017 Å) is associated with seven more or less discrete, red-degraded bands, showing frequency differences of 1580 and 380 cm.$^{-1}$. The ground-state frequencies of nitrosyl chloride are given by Burns and Bernstein (*J. Chem. Phys.*, 1950, **18**, 1669) as 1799 cm.$^{-1}$ (a stretching vibration mainly localized in the O–N bond), 592 cm.$^{-1}$ (a stretching vibration mainly localized in the N–Cl bond), and 332 cm.$^{-1}$ (bending). The 1580-cm.$^{-1}$ upper-state frequency can only well correspond to the 1799-cm.$^{-1}$ ground-state frequency. The 380-cm.$^{-1}$ upper-state frequency may represent either the 592- or 332-cm.$^{-1}$ ground-state frequency. Both the banded absorption ($\varepsilon_{max.} \sim 1$) and the shorter-wave-length visible absorption ($\varepsilon_{max.} \sim 5$) have very low intensity. While it is possible, therefore, that one of the systems corresponds to the 3900—3400-Å region for SO_2, assignment is quite uncertain. The 3900—3400-Å region for SO_2 has been interpreted as (20). These transitions may readily be re-formulated in terms of the symbols appropriate to the C_s symmetry of NOCl.

A much stronger region of continuous absorption has a maximum at about 1900 Å (Price and Simpson, 1941, *loc. cit.*). With increasing pressure, this absorption spreads somewhat to short wave-lengths and much more to long wave-lengths. Price and Simpson suggest it is the analogue of the 1600—1350-Å system for NO_2 and the 2400—1800-Å system

for SO_2. In terms of the present assignments the former analogy cannot be very close, since the analogue of the $(a_1'-\bar{\pi}_u)$ orbital is completely filled in the ground state of NOCl. Closer analogies are likely to be found with other 18-electron rather than with 17-electron molecules. We agree with Price and Simpson that the 1900-Å region of NOCl is probably analogous to the 2400—1800-Å system of SO_2. Its interpretation is therefore probably analogous to some of the transitions (24) to (27). Like the SO_2 system, the absorption is quite strong, $\varepsilon_{max.}$ being >2000 (Goodeve and Katz, *loc. cit.*).

Between the absorption in the visible region and that of the 1900-Å system, a broad maximum of absorption occurs (see Goodeve and Katz, *loc. cit.*), some of which may represent transition (21).

(xiii) CF_2. An uncondensed discharge through the vapour of a fluorocarbon gives rise to an extensive emission spectrum of many-headed bands lying between 2340 and *ca.* 5000 Å. A vibrational analysis of the shorter-wave-length end of this system has been made by Venkateswarlu (*Phys. Review*, 1950, **77**, 676) and the transition was assigned to the molecule CF_2. The analysis, and also the presence of both *J*- and *K*-rotational structure, of the bands shows, as expected from the present considerations, that the molecule is not linear. The frequencies of the sub-heads (*i.e.*, the *K*-structure) fit the relation expected for parallel bands.

Laird, Andrew, and Barrow (*Trans. Faraday Soc.*, 1950, **46**, 803) have observed some of the same bands in absorption between 2350 and 2650 Å. This establishes that the lower state is the ground state, so that the polarization of the transition identifies it as $^1B_2 \leftarrow\!\!- {}^1A_1$. The vibrations to appear in the emission transition are the two that are totally symmetrical (ν_1 and ν_2). It follows that $^1B_2$ is the symmetry of the electronic part of the upper-state wave function. The vibrational structure then agrees with the transition being an electronically allowed one. In absorption, the bands form a single progression with successive excitation of the bending vibration in the upper electronic state (495·5 cm.$^{-1}$ compared with 666·5 cm.$^{-1}$ in the ground state). This makes it clear that the apex angle changes considerably during the transition. Venkateswarlu found the *K*-structure of the bands to be shaded towards the violet, while the *J*-structure is shaded towards the red. This implies that the apex angle is larger in the upper than in the ground state; the question whether the bond length has increased or decreased must be left open. The existence, in the emission spectrum, of a long progression involving the symmetrical stretching frequency (1162 cm.$^{-1}$ in the ground state, 750 cm.$^{-1}$ in the upper state) but with the first and second bands the strongest indicates that the change of bond length is appreciable but not large.

Considering only the transitions so far formulated for an 18-electron molecule, we find only one—*viz.*, (27)—that is a parallel transition and leads to an increase of apex angle. It may therefore be that the transition just described is to be interpreted as (27). On the other hand, one would not expect (27) to lead to a very marked increase of apex angle. There is another possibility not so far formulated; it is (see the Figure)

$$\cdots(a_1')(\bar{b}_2'),\ ^1B_2 \leftarrow\!\!- \cdots(a_1')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where $(\bar{b}_2')$ represents the $(\bar{b}_2' - \bar{\sigma}_u)$ orbital. This should lead to a marked increase of both apex angle and bond length. Mulliken (quoted by Venkateswarlu) has earlier suggested this assignment. If correct, it means that there should be several longer-wave-length systems of CF_2. Weak bands on the long-wave-length side (3700—3300 Å) of the main part of the above emission system may represent one of these additional systems.

(xiv) ClO_2. Chlorine dioxide is a 19-electron molecule. According to the Figure its ground state should be $^2B_1$.

In absorption, the molecule possesses an extensive system of red-degraded absorption bands lying between 5225 and 2600 Å (Coon, *Phys. Review*, 1940, **58**, 926L; *J. Chem. Phys.*, 1946, **14**, 665). The (000) $\leftarrow$ (000) band is at 21,016 cm.$^{-1}$ and $\lambda_{max.}$ is at *ca.* 3300 Å. The transition is a strong one ($\varepsilon_{max.}$ at least 2000; Goodeve and Stein, *Trans. Faraday Soc.*, 1929, **25**, 738) and is therefore to be regarded as electronically allowed. Rotational analysis of the bands (Coon, 1946, *loc. cit.*) shows them to be of parallel type. Of the

longest-wave-length group of expected allowed transitions there are only two of parallel type. These may be formulated

$$\cdots(a_2'')(b_2')^2(a_1')^2(b_1'')^2,\ ^2A_2 \longleftarrow \cdots(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^2B_1 \quad . \quad . \quad (29)$$

$$\cdots(b_2')(a_1')^2(b_1'')(\bar{a}_1'),\ ^2A_2 \longleftarrow \cdots(b_2')^2(a_1')^2(b_1''),\ ^2B_1 \quad . \quad . \quad . \quad (30)$$

Transition (29) should cause a small decrease, and (30) a small increase, of apex angle. Both should cause a considerable increase of Cl–O distance and should occupy a fairly extensive region of the spectrum. Coon (1940, *loc. cit.*) points out that twenty or more bands due to the symmetrical stretching vibration appear in the transition, but not more than two of the symmetrical bending vibration; this indicates a much more profound change of Cl–O length than of OClO angle. The magnitude of both the breathing and the bending frequency is reduced from the ground state to the upper state (945 to 708, and 447 to 290 cm.$^{-1}$, respectively). Further, the rotational analysis reveals that both *K*- and *J*-structure degrade to the red at approximately the same rate. This confirms that the change of length is more important than that of angle. Coon showed in fact that, while the Cl–O distance increased markedly, there was a small decrease in apex angle. (The figures given for the angle were 109° ± 3° in the ground state and 92° ± 6° in the upper state; but these were based upon an old electron-diffraction value for the Cl–O bond length and are subject to correction.) The observed characteristics of the system thus fit with assignment to (29). Mulliken earlier came to the same conclusion. Assignment to (29) makes the electron jump analogous to that supposed responsible for the SO_2 3400—2600-Å bands. It should be noted, however, that the latter bands are considerably weaker.

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468. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part III.** HAB *and* HAAH *Molecules.*

By A. D. WALSH.

The electronic orbitals possible for bent and linear HAB and HAAH molecules are correlated. Whether or not a given orbital becomes more or less weakly bound as the molecule is changed from the bent to the linear form is discussed. The results are used to interpret the shapes and spectra of HAB and HAAH molecules and radicals. HAB molecules containing 10 or less valency electrons should be linear in their ground states. Molecules with 10—14 electrons should be bent in their ground states. 16-Electron HAB molecules should be linear again.

HAAH molecules containing 10 valency electrons should be linear in their ground states. Those containing 12 electrons should be bent but planar (*cis*- and *trans*-forms). Those containing 14 electrons should be bent and non-planar. The spectra of the isoelectronic molecules HCN and C_2H_2 are particularly discussed; the first excited state of each should be non-linear.

Orbitals of HAB *Molecules.*—The lowest-energy orbitals of a linear HAB molecule may be approximately described as follows, on the assumption that they are built solely from *s* and *p* atomic orbitals: (i) An *s* orbital on B. It is assumed that this plays no direct part in the binding of A to B and remains largely unchanged whatever the HAB angle. (ii) A σ orbital binding the H and the A atom. It is built from an H 1*s* and an A *sp* hybrid valency. (iii) A σ orbital binding the B and the A atom. It is assumed to be built from an A *sp* hybrid valency and a B pure *p* valency. (iv) A π orbital binding the B and the A atom. It is built by the in-phase overlap of *p* orbitals on A and B. It is two-fold degenerate; and, since in many HAB molecules B is of greater electronegativity

* Part II, preceding paper.

than A, it is usually more localized on B than on A. (v) A $\bar{\pi}$ orbital that is anti-bonding between A and B. It is built by the out-of-phase overlap of p orbitals in A and B. It is two-fold degenerate and, by the arguments of Part II, usually more localized on A than on B. (vi) A σ orbital built by the out-of-phase overlap of an orbital on A with a B $p\sigma$ and the H 1s valency. It will usually be more localized on A than on B or H. It is analogous to the $\bar{\sigma}_g$ orbital described in Part II and therefore is assumed to be built from an s orbital of A.

The lowest-energy orbitals of a bent HAB molecule, in addition to the s lone-pair orbital on B, can be approximately described as follows: (i) An a' orbital binding the H and the A atom. When the HAB angle is 90°, the orbital is built from an H 1s and an A pure p valency. (ii) An a' orbital binding the A and the B atom. In the 90° molecule, it is built by the in-phase overlap of pure p valencies on A and B, pointed towards each other. In Fig. 1 the orbitals of the bent and the linear HAB molecules are correlated. Clearly, the two bonding a' orbitals must become the two σ orbitals; and, as explained in Parts I and II, the a'–σ curves must fall from left to right. (iii) An a'' orbital binding the A and the B atom and built by the in-phase overlap of a p orbital on A and a p orbital on B, the axes of these p orbitals being perpendicular to the molecular plane. Clearly, this orbital must become one of the bonding π orbitals in the linear molecule. There is no reason why it should change appreciably in binding energy as the HAB angle changes. It is therefore represented in Fig. 1 by a horizontal straight line. (iv) An a'' orbital that is built by the out-of-phase overlap of p orbitals on A and B, their axes being perpendicular to the molecular plane. It is anti-bonding between A and B, and becomes one of the anti-bonding $\bar{\pi}$ orbitals in the linear molecule. Like the other a'' orbital, there is no reason why its binding energy should change appreciably as the HAB angle changes. It is therefore represented in Fig. 1 by a horizontal straight line. (v) An $\bar{a}'$ orbital analogous to the $\bar{a}_1'$ orbital of Part II. By analogy with the latter, when the HAB angle is 90°, the orbital is built from a pure p_z orbital on A overlapping out-of-phase with a B pa' and the H 1s valency. The z-axis lies in the plane of the molecule and bisects the HAB angle. The orbital is usually predominantly localized on A. As the apex angle increases, the orbital tends towards the $\bar{\sigma}$ orbital of the linear molecule. Since it is largely a p orbital of A in the 90° molecule, but an s orbital of A in the linear molecule, it is represented in Fig. 1 by a line that falls steeply from left to right. (vi) An orbital which in the 90° molecule is a pure s lone pair orbital on A. It is of species a', here written $a's_A$. As the HAB angle changes towards 180° the orbital becomes increasingly built from a p orbital of A whose axis lies in the molecular plane. It is therefore represented in Fig. 1 by a line that rises steeply from left to right. Being localized largely on A, it tends to become one of the $\bar{\pi}$ (rather than one of the π) orbitals of the linear molecule. As the HAB angle approaches 180° it becomes, to some extent, A$\leftrightarrow$B anti-bonding. If the $\bar{\sigma}$ lies slightly lower than the $\bar{\pi}$ orbital, the $a's_A$ orbital curve will actually lead to the $\bar{\sigma}$ rather than to the $\bar{\pi}$ orbital. There is every expectation, however, that this is not so and that $\bar{\sigma}$ lies above $\bar{\pi}$. In the diatomic molecules isoelectronic with HAB molecules (*e.g.*, N_2 isoelectronic with HCN) the analogous $\bar{\sigma}$ orbital certainly lies above the analogous $\bar{\pi}$ orbital. Moreover, analysis (see below) of the spectrum of C_2H_2 (also isoelectronic with HCN) fits well with the assumption that $\bar{\pi}$ lies below $\bar{\sigma}$. For these reasons and also on grounds of simplicity Fig. 1 is drawn with $\bar{\sigma}$ above $\bar{\pi}$. (vii) An a' orbital which in the 90° molecule is a nearly pure p orbital on B whose axis lies in the molecular plane but perpendicular to the A–B line. It probably has a sufficiently different binding energy from the $a's_A$ orbital (or to the two bonding a' orbitals) for little interaction to occur. As the HAB angle increases towards 180°, this a' orbital interacts more and more with the orbital which at 90° is $a's_A$ because the latter becomes increasingly built from a p orbital of A. This interaction increases the binding energy of the present a' orbital. In other words, the present a' orbital becomes increasingly A$\leftrightarrow$B bonding as the apex angle increases and is represented in Fig. 1 by a line that descends from left to right. At 180° the orbital becomes one of the bonding π orbitals.

Fig. 1 shows the eight lowest-lying intra-valency-shell orbitals. A ninth, highest, is also possible but is not needed for the purposes of this paper; see also the comments on this point in Part I.

Shapes of HAB *Molecules.*—The lowest five orbital curves in Fig. 1 either fall from left to right or are horizontal. One therefore expects that HAB molecules containing 10 or less valency electrons will be linear in their ground states. HCN, containing 10 valency electrons, is an example. The hypothetical molecules HBO and HBeF should also be linear. The HCO radical, however, containing 11 valency electrons, has to have one electron in the $a's_A$–$\bar{\pi}$ orbital. By analogy with NO_2 (see Part II), the radical should therefore possess an apex angle in its ground state appreciably less than 180°. A spectrum has been attributed to HCO which we discuss below in relation to the shape of the radical. The 12-electron radical HON or HNO (which has been postulated as an intermediate in the photochemical decomposition of nitrites; see, *e.g.*, Thompson and Dainton, *Trans. Faraday Soc.*, 1937, **33**, 1546) must in its ground state have two electrons in the $a's_A$–$\bar{\pi}$ orbital. It should therefore possess a ground-state apex angle appreciably less than that for HCO. The HO_2 radical, with

FIG. 1.

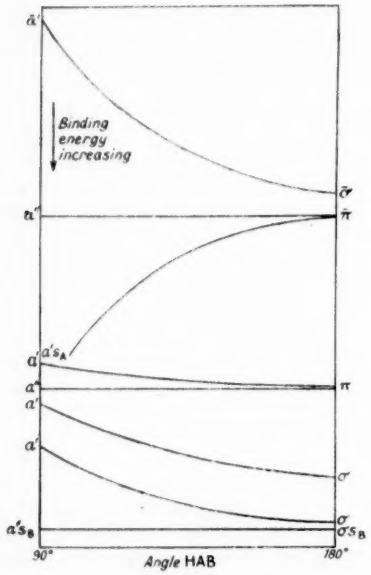
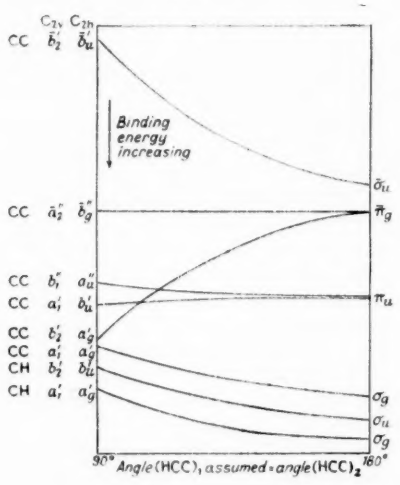


FIG. 2.



13 valency electrons, should also be non-linear with an apex angle in the ground state not much less than that of HNO. Of 14-electron molecules, HOCl and HOBr are almost certainly bent molecules in the ground state, in accord with expectations from Fig. 1.

The first excited state of HCN should be bent, just as should be the first excited state of ClCN or CO_2 (Part II). The low-lying excited state of HCO in which the outermost electron lies in the a''–$\bar{\pi}$ or $\bar{a}'$–$\bar{\sigma}$ orbital rather than in the $a's_A$–$\bar{\pi}$ orbital should have an equilibrium form that is linear.

The ground states of 16-electron molecules should be linear once again. The molecule $(HFF)^-$ would thus be expected to be linear. Although the shape of this particular ion is not known, it is of interest that the shape of the isoelectronic ion $(FHF)^-$ is almost certainly linear and symmetrical (Westrum and Pitzer, *J. Amer. Chem. Soc.*, 1949, **71**, 1940).

Reactivity of HAB *Molecules.*—The reactivity of HAB molecules or radicals may be discussed along lines similar to those used in Part II. The HCO radical in its ground state, for example, should have its odd electron largely localized on the C atom. The first excited state of the HCN molecule should have an odd electron largely localized on the C atom and another largely localized on the N atom.

Spectra of HAB *Molecules.*—(1) *Spectrum of* HCN. If triplet ← singlet changes are

neglected, the longest-wave-length absorption regions of HCN, if the upper state remains linear, should be due to the transitions

$$\cdots(\pi)^3(\pi),\ ^1\Delta \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\cdots(\pi)^3(\bar{\pi}),\ ^1\Sigma^- \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\cdots(\pi)^3(\bar{\pi}),\ ^1\Sigma^+ \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Transitions (1) and (2) are electronically forbidden, but (3) is allowed. Transition (1) is two-fold degenerate. In fact, one can see from Fig. 1 that two of the transitions should lead to strongly bent upper states and two to linear upper states; and further that it is the two transitions that lie lowest in energy that should lead to the bent upper states. These two will be

$$\cdots(a'')^2(a')(a'),\ ^1A' \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\cdots(a'')(a')^2(a'),\ ^1A'' \longleftarrow \cdots(\pi)^4,\ ^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Since, by analogy with atoms and diatomic molecules, $^1\Delta$ may be expected to lie lower than $^1\Sigma^-$ and $^1\Sigma^+$, one may suggest that (4) and (5) correlate with the degenerate transition (1). Transitions (4) and (5) are electronically allowed, though likely to be weak because of the Franck–Condon principle and because of their relation to (1). Transition (2) is likely to be so weak as not to be observed. Transition (3), being of the $V \longleftarrow N$ class, is expected to be intense. All four transitions should lead to a marked increase of C–N length. Transitions (4) and (5) should thus lead to the appearance of both the bending and C–N stretching vibrations in the upper state; transition (3) should lead to the appearance only of the C–N stretching vibration. The magnitude of the stretching frequency should be considerably reduced relatively to that of the ground state. Let us now compare these expectations with the observed spectrum.

The absorption system of longest wave-length lies between 2000 and 1789 Å (Hilgendorff, *Z. Physik*, 1935, **95**, 781). It is weak and consists of bands with a mean separation of 450 cm.$^{-1}$. It has not yet been properly analysed, but may be attributed to (4) and/or (5). 450 cm.$^{-1}$ may represent the bending frequency (712 cm.$^{-1}$ in the ground state) in the upper state, but the C–N stretching frequency ought to be present also. The second absorption system is much stronger. It begins around 1500 Å and extends to at least 1350 Å (Price, *Phys. Review*, 1934, **46**, 259; Price and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 381). At the long-wave-length end it consists of quite sharp bands which are single-headed and shaded towards the red. The bands steadily increase in intensity up to the shortest-wave-length band at *ca.* 1360 Å. Price reported that the main bands were reproduced very well by the formula

$$\nu = 68{,}645 + 901(v' + \tfrac{1}{2}) - 22(v' + \tfrac{1}{2})^2 \ *$$

The intensity of the 1500—1350-Å system (a little weaker than the Rydberg bands at shorter wave-lengths) makes it practically certain that it is to be identified as transition (3). The facts that only one vibration frequency appears strongly in the system, that the bands are red-degraded and that there is a slow rise to maximum intensity accord with our expectations for transition (3). The single-headed nature of the bands is also in accord with the expectations for (3), since the bands of (3) should possess no *Q*-branch. Clearly the frequency 901 cm.$^{-1}$ is to be identified as the C–N stretching vibration in the upper state. This vibration has a frequency of 2089 cm.$^{-1}$ in the ground state. The reduction is very great, but proportionately no greater than that known to occur for similar $(\bar{\pi}) \longleftarrow (\pi)$ jumps in, *e.g.*, the N_2 and the O_2 molecule. ω_e for the O_2 molecule drops from 1580 to 700 cm.$^{-1}$ in passing from the $X^3\Sigma_g^-$ to the $B^3\Sigma_u^-$ state. To interpret the 901-cm.$^{-1}$ frequency as the bending vibration ν_2 increased from the value of 712 cm.$^{-1}$ in the ground state would be difficult in view of the fact that only one frequency is strongly involved in the observed absorption—for whether a low-lying upper state is bent or not, it is expected to involve a strongly C$\longleftrightarrow$N anti-bonding orbital; so that while ν_1' might

* The origin, however, lies at longer wave-lengths than 1457 Å (68,645 cm.$^{-1}$). The bands can be followed to *ca.* 1500 Å (see photograph by Price and Walsh, *loc. cit.*).

occur alone, ν_2' is expected to occur only in association with ν_1'. Observation and theory agree in assigning a linear upper state to the 1500—1350-Å system.

(2) *Spectrum of* HCO. The longest-wave-length absorption of the HCO radical should be due to one of the transitions

$$\cdots(a''),\ ^2A'' \longleftarrow \cdots(a'),\ ^2A' \quad \ldots\ldots\ (6)$$

$$\cdots(a')(a')^2,\ ^2A' \longleftarrow \cdots(a')^2(a'),\ ^2A' \quad \ldots\ldots\ (7)$$

Both are allowed transitions, (6) with polarization perpendicular to the molecular plane, (7) with polarization in the molecular plane. Transition (6) should cause an increase in apex angle (to a linear upper state), (7) a decrease. Transition (6) would be better formulated as

$$\cdots(\bar{\pi}),\ ^2\Pi \longleftarrow \cdots(a'),\ ^2A' \quad \ldots\ldots\ (8)$$

Transition (7) should cause a particular increase of C–O distance, but (8) would probably also cause an increase. Both transitions should therefore involve both the bending and a stretching vibration.

The so-called "hydrocarbon flame bands" observed between 4100 and 2500 Å (maximum intensity between 3600 and 3000 Å) in the emission spectra of certain flames have been attributed by Vaidya (*Proc. Roy. Soc.*, 1934, *A*, **147**, 513) to the HCO radical. Dyne and Style (*Discuss. Faraday Soc.*, 1947, 159) have obtained the bands in fluorescence by exciting gaseous formaldehyde with light of wave-length in the fluorite region; this supports the identification of the emitter as HCO. The identification is not yet fully proved, but will be provisionally assumed here. Gaydon ("Spectroscopy and Combustion Theory," Chapman and Hall, London, 1948), from a study of the rotational fine structure of the band, has concluded that the emitter is linear or nearly so. The conclusion, if accepted, must be taken as referring to the equilibrium forms of both upper and lower states. Vaidya has classified the bands into two systems, *A* and *B*, which appear under slightly different experimental conditions. The bands of the *B* system are mostly separated from the strongest *A* bands by intervals of about 240 and 154 cm.$^{-1}$. Gaydon, however, doubts the reality of two separate systems, suggesting instead that the *A* and the *B* bands are different heads of the same bands. According to Gaydon, the main vibrational frequencies involved are 1072 cm.$^{-1}$ (in the upper state) and *ca.* 1960 cm.$^{-1}$ (in the lower state). On the other hand, Murphy and Schoen (*J. Chem. Phys.*, 1951, **19**, 1214) have shown that all but five of the bands reported by Vaidya may be expressed in terms of two vibrations, *i.e.*, four frequencies, two in the upper and two in the lower state. These are: $\nu_1' = 1229$ cm.$^{-1}$; $\nu_2' = 1070$ cm.$^{-1}$; $\nu_1'' = 1880$ cm.$^{-1}$; $\nu_2'' = 1538$ cm.$^{-1}$. v_1'' is found to have any value up to 9; v_2'' is always 0 or 1. Comparison of the lower-state frequencies with those of HCHO suggests that ν_1 represents the C=O valency vibration (1744 cm.$^{-1}$ in the ground state of HCHO) and ν_2 represents the CH bending vibration (1503 cm.$^{-1}$ in the ground state of HCHO). If these analyses and the ascription of the bands to HCO are confirmed, the characteristics are not incompatible with the expectations for the reverse of transition (8). The expectations for the reverse of transition (7) would also fit, except for the supposed linearity of the upper state.

Vaidya compares the bands with those of the β-system of the isoelectronic molecule NO. The β emission bands of NO lie in the same region of the spectrum as the hydrocarbon flame bands. (They also reveal closely similar vibrational frequencies, *viz.*, 1038 and 1904 cm.$^{-1}$, but if the Murphy–Schoen identification of the 1070-cm.$^{-1}$ frequency is accepted, its closeness to 1038 cm.$^{-1}$ is fortuitous.) The bands are known to represent a $^2\Pi \leftrightarrow ^2\Pi$ transition and may be interpreted as involving the jump of an electron from a $(\bar{\pi})$ to a (π) orbital. The parallel, such as it is, would fit better with assignment of the bands to the reverse of transition (7) than to the reverse of transition (8). The supposed long progressions in ν_1'' and the big reduction of ν_1' relative to ν_1'' would fit the reverse of (7) better than the reverse of (8).

The observed bands are, however, not yet proved to be due to HCO; nor is the analysis so far given yet to be accepted without reserve. If the provisional analysis or identity of the emitter should be incorrect, the present remarks will still be of value in predicting the

characteristics to be expected for any long-wave-length transitions observed for the HCO radical.

(3) *Spectrum of* HO_2. Although no electronic transition has yet been attributed to HO_2, it is worth noting that the radical should possess at least one low-lying transition. This may be formulated in absorption as

$$\cdots (a')(a'')^2,\ ^2A' \longleftarrow \cdots (a')^2(a''),\ ^2A'' \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It should be an allowed transition with polarization perpendicular to the molecular plane, and should cause an increase of apex angle.

Orbitals and Spectra of HAAH *Molecules.*—The HCN molecule is isoelectronic with C_2H_2. In order to discuss the spectrum of the latter, let us first consider the orbitals appropriate to HAAH molecules as a class. Such molecules may be linear or non-linear. If the latter, but still planar, they may be either *cis* or *trans*. *cis*-Molecules would belong to the C_{2v}, *trans* to the C_{2h} class. The symbols appropriate to the orbitals of the latter are

	C_2^z	σ_h	i		C_2^z	σ_h	i
a_g	+	+	+	b_g	−	−	+
a_u	+	−	−	b_u	−	+	−

where i represents the operation of inversion at the centre of symmetry of C_{2h} molecules. C_2^z represents the operation of rotation by 180° about the z axis which is taken as passing through the centre of symmetry and at right angles to the molecular plane. σ_h represents the operation of reflection in the plane of the molecule. + and −, as usual, imply that the wave function does not or does, respectively, change sign when a particular operation is carried out. The C_{2v} symbols have been defined in Part I. For convenience we shall add single and double primes to the symbols for both classes to denote symmetric and anti-symmetric behaviour with respect to reflection in the plane of the molecule.

Now the lowest-energy orbitals of a linear HAAH molecule are, in order or decreasing binding energy, σ_g, σ_u, σ_g, π_u, $\bar{\pi}_g$, $\bar{\sigma}_u$. The first two σ orbitals may be thought of as largely localized in the AH bonds. The third and fourth σ orbitals and both the π orbitals are AA orbitals. Whether we correlate the orbitals of the linear molecule with those of a bent C_{2v} (*cis*-)molecule or with those of a bent C_{2h} (*trans*-)molecule, it is easy to see that, just as one of the curves leading to $\bar{\pi}$ in Fig. 1 rises from the bent to the linear HAB molecule, so one of the curves leading to $\bar{\pi}_g$ will rise from the bent to the linear HAAH molecule. This is because the orbital concerned changes from being built from s orbitals of the A atoms in a bent molecule where the HCC angles are 90° to being built from p orbitals of the A atoms in the linear molecule. Further, by a simple application of the principles used in these papers it is not difficult to show that the five lowest orbital curves on a correlation diagram for bent-linear molecules will have their minima on the HCC angle = 180° line. Fig. 2 shows the correlation diagram that one obtains.* In other words, HAAH molecules containing 10 valency electrons should have linear ground states while those containing 11 or 12 valency electrons should have non-linear ground states. The latter might be either *cis* or *trans*. In agreement, the C_2H_2 molecule, possessing 10 valency electrons, has a linear ground state. The HNNH molecule, having 12 valency electrons, would be expected to have a bent ground state, existing in either a *cis*- or a *trans*-form. The correctness of the expectation is strongly supported by the fact that the molecule N_2F_2 is known to have a planar ground state with *cis*- and *trans*-isomers (Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46). From Fig. 2 one would also expect 14-electron molecules to have bent ground states. Such ground states, however, would have the anti-bonding b_g''–$\bar{\pi}_g$ orbital filled; and, in order to relieve the repulsion represented by this anti-bonding orbital, one-half of the molecule would be expected to be twisted through 90° relative to the other, *i.e.*, into a non-planar form. The reason for this twisting has been described earlier (Walsh, *J.*, 1948, 331) and will be referred to again in Part IX. The expectation is strongly supported by the observed shape of the ground state of the H_2O_2 molecule which contains 14 valency electrons.

* It should be noted that for acetylene, if $\bar{\sigma}_u$ lay below $\bar{\pi}_g$, crossing of the orbital curves leading to these two orbitals would be possible; this is in contrast to the situation in, *e.g.*, AB_2 molecules. However, there is little doubt that $\bar{\sigma}_u$ lies above $\bar{\pi}_g$ for acetylene.

Turning now to the spectrum of C_2H_2, it is clear that the longest-wave-length absorption should lead to a bent upper state, just as with the isoelectronic molecule HCN. The longest-wave-length absorption known consists of very weak, red-degraded bands [$\varepsilon_{max.} \simeq 0{\cdot}3$ (Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466)] between 2400 and 2100 Å. Kistiakowsky (*Phys. Review*, 1931, **37**, 276) observed bands from 2377 to 2246 Å. Lind and Livingston (*J. Amer. Chem. Soc.*, 1933, **55**, 1036) observed sharply defined bands stretching to shorter wave-lengths. Since this paper was submitted for publication, King and Ingold (*Nature*, 1952, **169**, 1101) have reported that the absorption does lead to a non-linear upper state; that, in fact, the excited state has a planar, centrosymmetric, zigzag form; that the lowest vibrational level lies at 2369 Å; that the upper-state vibration frequencies involved are 1385 (CC stretching) and 1049 cm.$^{-1}$ (opening the HCC angles); and that the transition is polarized perpendicularly to the plane of the bent molecule (implying that the upper state has the symmetry A_u of the C_{2h} class).

What are the detailed expectations concerning the longest-wave-length transition? Neglecting triplet ⟵ singlet transitions, we should expect, if the upper state remained linear, the four lowest-energy transitions to be

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Delta_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Sigma_u^- \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\cdots(\pi_u)^3(\bar{\pi}_g),\ {}^1\Sigma_u^+ \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Transition (10) would be two-fold degenerate and, like (11), would be electronically forbidden. From Fig. 2, however, it is clear that two of the four transitions should in fact lead to bent upper states. These two will be the two of lowest energy. If the bent upper states are taken to be *trans*, the formulation of the transitions should be

$$\cdots(b_u')(a_u'')^2(a_g'),\ {}^1B_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\cdots(b_u')^2(a_u'')(a_g'),\ {}^1A_u \longleftarrow \cdots(\pi_u)^4,\ {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Both are electronically allowed. ${}^1\Delta_u$ correlates with ${}^1B_u$ and ${}^1A_u$; ${}^1\Sigma_u^-$ with ${}^1A_u$, and ${}^1\Sigma_u^+$ with ${}^1B_u$. The observed ${}^1A_u \longleftarrow {}^1\Sigma_g^+$ transition is to be identified as (14). Transition (14) is electronically allowed (with polarization along the z axis), but it should be weak partly because of the Franck–Condon principle and partly because of its relation to the forbidden transition (10) or (11). It should weaken the C–C bond as well as reduce the HCC angles and so should arouse both the CC stretching vibration and one of the bending vibrations of the molecule. The CC stretching frequency should be reduced relatively to its ground state value (1974 cm.$^{-1}$). All these expectations accord with the facts.

It is of particular interest that the bending frequency (1049 cm.$^{-1}$) is increased in the excited, relatively to the ground, state. $\nu_4''\pi_g$ of the ground state carries the molecule into the bent, *trans*-form (C_{2h}) and has a value 612 cm.$^{-1}$. This is in accord with the upper state's resembling a C_2H_4 molecule minus two H atoms; for the force constants controlling bending of C–H bonds are known to increase from C_2H_2 to C_2H_4,* a fact readily understandable in terms of the carbon-atom hybridization involved and the spherical symmetry of an *s*-orbital, unlike that of a *p*-orbital.

By analogy with atoms and diatomic molecules, one would expect ${}^1\Delta_u$ to lie lower than ${}^1\Sigma_u^-$ and ${}^1\Sigma_u^+$. In that case the observed ${}^1A_u$ state probably correlates with ${}^1\Delta_u$ rather than ${}^1\Sigma_u^-$; and we should expect to observe two further intra-valency-shell transitions, *viz.*, transition (13) to a bent upper state and (at shorter wave-lengths) transition (12) to a linear upper state. The forbidden transition (11) would probably be too weak to appear. Transition (12), belonging to the $V \longleftarrow N$ class, should be more intense than (13). The latter however, is electronically allowed and polarized in the plane of the bent molecule; it should arouse both CC stretching and HCC bending frequencies. Transition (12) should arouse strongly only the totally symmetrical CC stretching frequency, considerably

* Linnett, Heath, and Wheatley (*Trans. Faraday Soc.*, 1949, **45**, 833) give the following values >C–H 0·66 × 10^{-11}, $=C\!\!<_{H}$ 0·60 × 10^{-11} (in-plane distortion), and ≡C–H 0·24 × 10^{-11} erg/radian^2.

reduced from its value of 1974 cm.$^{-1}$ in the ground state. By analogy with HCN, the reduction might be to a value ≃800 cm.$^{-1}$. The frequency should be much less in the $^1\Sigma_u^+$ than in the ^1A_u or the ^1B_u state since the a_g'–$\bar{\pi}_g$ orbital loses some of the anti-bonding character which it has in the linear molecule, tending towards a bonding orbital in the 90° bent molecule. On the other hand, Ross (*Trans. Faraday Soc.*, 1952, **48**, 973), as a result of theoretical calculations, has suggested that the observed ^1A_u state correlates with $^1\Sigma_u^-$ rather than with $^1\Delta_u$. In that case, the $^1\Delta_u$ state remains linear and transition to it, being forbidden, would probably not be observed; and we should expect to observe only one further intra-valency-shell transition, *viz.*, (13) to a bent upper state correlating with $^1\Sigma_u^+$. One difficulty with Ross's suggestion is that it implies that the order of the $^1\Delta$ and the $^1\Sigma$ state is different for C_2H_2 and HCN; if $^1\Delta$ lay above $^1\Sigma$ for HCN, then the upper state of the $^1\Sigma \longleftarrow {}^1\Sigma$ transition, to which the HCN 1500—1350-Å bands undoubtedly correspond, should be bent and it would be difficult to explain why only one frequency appears strongly in the region.

King and Ingold were unable to follow the bands of transition (14) to their maximum, since the latter lay outside the range observable with a quartz spectrograph. According to Ross (*loc. cit.*) the maximum would probably occur between 1900 and 1650 Å. If this estimate is correct, then, as the following evidence shows, the transition is overlapped by at least one other transition before its maximum is reached.

The Rydberg bands of acetylene start sharply near 1500 Å. To the long-wave-length side of them and to the short-wave-length side of the bands already mentioned, occurs at least one other system. The intervening bands (see photograph by Price and Walsh, *Trans. Faraday Soc.*, 1945, **41**, 381) cover an extensive region from *ca.* 2070 to *ca.* 1550 Å with $\lambda_{max.}$ at *ca.* 1725 Å. Platt, Klevens, and Price (*loc. cit.*) give $\varepsilon_{max.}$ for this region as ≃500 compared with a value between 10,000 and 100,000 for the first Rydberg band, but these values are subject to an uncertainty of at least three times. The author's photographs and appearance–pressure data suggest that $\varepsilon_{max.}$ for the 1725-Å system is not less than 10% of $\varepsilon_{max.}$ for the first Rydberg band. The comparatively high intensity makes it practically certain that, at least in the neighbourhood of $\lambda_{max.}$, a $V \longleftarrow N$ transition is involved. In other words, transition (12) is present at least around 1725 Å. In the longer-wave-length portion of the region (2070—1850 Å) the frequency intervals are 1365 and 865 cm.$^{-1}$ (Herzberg, *Trans. Faraday Soc.*, 1931, **27**, 378). By analogy with the 2400—2100-Å bands, these frequencies almost certainly represent CC stretching and HCC bending respectively. The fact that two frequencies are involved almost certainly implies that the upper state is bent; and the absorption may be identified as belonging to transition (13). To be sure, other bands are present weaker than those concerned in the 1365- and 865-cm.$^{-1}$ frequency intervals (Walsh, unpublished results), but these may well represent the expected continuation of the 2400—2100-Å system. Some at least of the bands are red-degraded. The pattern of bands observed in the 2070—1850-Å region stretches some way further to short wave-lengths, but towards 1725 Å it becomes confused and not obviously the same as at longer wave-lengths. A frequency difference of *ca.* 720 cm.$^{-1}$ is noticeable towards the shorter-wave-length end of the region. The diffuseness of the bands, the presence of emission lines in the Lyman continuum used as background in the author's photographs, and the overlapping of bands make both measurement and analysis difficult. While certainty must await a complete analysis of the region, it appears not unlikely that two main transitions are concerned in the 2070—1550-Å region: one that stretches from the 2070—1850-Å region towards shorter wave-lengths and so occupies a very extensive region of the spectrum, and one (more intense) that overlaps this in the neighbourhood of 1725 Å. It is noteworthy that, on intensity data, Platt, Klevens, and Price (*loc. cit.*) show the 2070—1850-Å region as a separate transition about 100 times weaker than that in the 1725-Å region. It appears therefore that $^1\Delta_u$ lies lower than $^1\Sigma_u^-$ and $^1\Sigma_u^+$; that the 2400—2100-Å bands represent transition to a bent ^1A_u state correlating with $^1\Delta_u$; that the 2070—1850-Å bands represent transition to a bent ^1B_u state correlating with $^1\Delta_u$;* and

* Herzberg (*loc. cit.*) suggested the bands were due to a $^3\Sigma \longleftarrow {}^1\Sigma$ transition, but this is unlikely.

that in the neighbourhood of 1725 Å appears transition (12) [overlapping (13)] to a linear $^1\Sigma_u^+$ upper state, the bands being analogous to the HCN 1500—1350-Å system and presumably involving a single strong progression. The alternative interpretation, based on Ross's suggestion, *viz.*, that the whole 2070—1550-Å region represents one transition appears less likely. The possibility of complications such as the existence of transitions to *cis* upper states should, however, be borne in mind; it would certainly be expected that *cis*- and *trans*-isomers of bent C_2H_2 would exist. It should also be noted that Herzberg (*loc. cit.*) refers to weak continuous absorption setting in at *ca.* 1880 Å; the origin of this is unknown, but may be impurity.

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469. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part IV.* Tetratomic Hydride Molecules,* AH_3.

By A. D. WALSH.

The orbitals of planar and pyramidal AH_3 molecules are correlated. A figure is plotted to indicate whether a given orbital rises or falls in energy as the HAH angle is increased. This is used to explain and predict (i) the shapes and (ii) the spectra of AH_3 molecules. In their ground states, AH_3 molecules containing not more than 6 valency electrons should be planar, and molecules containing 7 or 8 should be pyramidal.

Electronic Orbitals of AH_3 *Molecules.*—The symbols used to describe the orbitals possible for a planar AX_3 molecule (D_{3h} symmetry) are as follows:

	Operation			
Symbol	C_3	$C_2(y)$	σ_h	$\sigma_v(y)$
a_1'	+	+	+	+
a_1''	+	+	−	−
a_2'	+	−	+	−
a_2''	+	−	−	+
e'	} Two-fold degenerate orbitals		{ +	
e''			{ −	

The z axis is taken as passing through atom A and as being perpendicular to the molecular plane. C_3 denotes a rotation by 120° about this axis. $C_2(y)$ denotes a rotation by 180° about one of the A–H lines. σ_h denotes a reflection in the molecular plane. $\sigma_v(y)$ denotes a reflection in a plane containing the z-axis and one of the A–H lines. + and − denote, respectively, that the wave function does not or does change sign when subjected to the symmetry operation in question. The signs in the last column are fixed by the signs in the first three; the last column is therefore redundant, but is included to facilitate comparison with the symbols for pyramidal molecules. The symbol e is used for all two-fold degenerate orbitals. Single and double primes denote, respectively, orbitals that are symmetric and anti-symmetric with respect to reflection in the molecular plane.

The symbols used to describe the orbitals possible for a pyramidal molecule AX_3 (C_{3v} symmetry) are as follows:

Symbol	C_3	$\sigma_v(y)$
a_1	+	+
a_2	+	−
e	Two-fold degenerate orbitals	

The z axis passes through atom A and is perpendicular to the plane of the three H atoms. C_3 and $\sigma_v(y)$ have the same meanings as before. Note that an a_2'' orbital of the planar molecule becomes an a_1 orbital of the pyramidal molecule, a_1' becomes a_1, a_1'' becomes a_2, and a_2' becomes a_2.

The lowest-energy electronic orbitals possible for a planar AH_3 molecule may be

* Part III, preceding paper.

described as follows: (i) Three orbitals binding the H atoms to the central atom. Each of these may, for discussions of molecular shape, be regarded as localized in a particular A–H distance and formed by the in-phase overlap of a hydrogen 1*s* valency and an sp^2 hybrid valency of A. All three orbitals are symmetric with respect to reflection in the molecular plane. For discussions of spectroscopic transitions involving these orbitals, however, they must be regarded as non-localized. When so regarded, molecular symbols become appropriate. The equivalent, non-localized orbitals may be obtained as in-phase or out-of-phase combinations of one orbital with the other two (see Fig. 1). The group of three equal orbitals is then split. The first type of combination results in a single a_1' orbital. The second results in two degenerate e' orbitals, the two-fold degeneracy arising essentially from the two-fold symmetry of the potential field. The non-localized orbitals are described further below. (ii) An orbital localized on atom A, closely resembling a pure *p* orbital of A whose axis is perpendicular to the molecular plane. This orbital is of species a_2'' and is non-bonding. (iii) Three orbitals each anti-bonding in each A–H distance and symmetric with respect to reflection in the molecular plane. They are of species $\bar{a}_1'$, $\bar{e}'$, $\bar{e}'$, and are formed by the out-of-phase overlap of atomic orbitals on A with the H 1*s* atomic orbitals. The bars are added to the usual group symbols to denote the anti-bonding character. The lowest of the three is $\bar{a}_1'$. In it the three H orbitals are in-phase and the orbital is therefore bonding between the H atoms. The three H 1*s* orbitals overlap out-of-phase with the A *s* orbital. A radial node is thus present (see Fig. 2). In the $\bar{e}'$ orbitals two of the H 1*s* orbitals are in-phase with each other, the third being out-of-phase. These

FIG. 1. (*Choice of positions for nodal plane not unique.*)

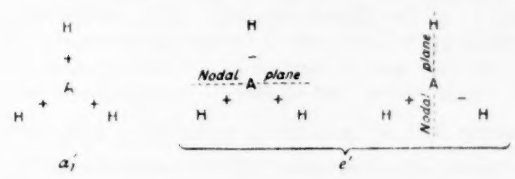


FIG. 2

orbitals are therefore anti-bonding, as a net effect, between the H atoms; and therefore lie above $\bar{a}_1'$ which, although, like the $\bar{e}'\bar{e}'$ orbitals, is A$\leftrightarrow$H anti-bonding, is also H$\leftrightarrow$H bonding.

For a pyramidal AH_3 molecule in which each HAH angle is 90°, the lowest-energy orbitals may be described as follows: (i) Three bonding orbitals. Each may be regarded as localized in a particular A–H distance and formed by the in-phase overlap of a hydrogen 1*s* orbital and a pure *p* orbital of A. With equal validity the orbitals may be regarded as non-localized and formed from combinations of the three localized orbitals. The non-localized orbitals comprise a single a_1 orbital (in-phase overlap of all three localized bonding orbitals) and two degenerate *e* orbitals (out-of-phase overlap of one of the localized bonding orbitals with the other two). Obviously, these three orbitals become the a_1' and two e' orbitals of the planar molecule. Since the localized orbitals are built from pure *p* orbitals of A in the 90° AH_3 molecule, but from sp^2 hybrid orbitals of A in the planar molecule, they become (as explained in previous papers of this series) more tightly bound as the HAH angle increases from 90° to 120°. For reasons made explicit below, the non-localized orbitals also become more tightly bound as the HAH angle increases. (ii) An orbital localized on atom A, closely resembling a pure *s* orbital of A. This is a non-bonding orbital of species a_1. Clearly, it must become the a_2'' orbital of the planar molecule. As the HAH angle increases from 90° to 120° the orbital becomes very much less strongly bound since it changes from an *s* to a *p* atomic orbital. (iii) Three anti-bonding orbitals of species $\bar{a}_1$, $\bar{e}$, $\bar{e}$, which become the anti-bonding $\bar{a}_1'$, $\bar{e}'$, $\bar{e}'$ orbitals of the planar molecule.

The various non-localized orbitals of the molecule can also be obtained by a procedure similar to that used in Part I. We form first the three possible combinations of the H 1*s* wave functions. These may be chosen as $1s_1 + 1s_2 + 1s_3$, $1s_1 - 1s_2$, and $1s_1 + 1s_2 - 1s_3$.

For simplicity the coefficients properly belonging to these orbitals are omitted. To form such H_3 group orbitals automatically takes account of the symmetry of the molecule. The components from which the non-localized molecular orbitals are built may then be written as follows:

Component	Symbol for C_{3v} symmetry	Symbol for D_{3h} symmetry	Component	Symbol for C_{3v} symmetry	Symbol for D_{3h} symmetry
$1s_1 + 1s_2 + 1s_3$	a_1	a_1'	p_z	a_1	a_2''
$1s_1 - 1s_2$	e	e'	p_x	e	e'
$1s_1 + 1s_2 - 1s_3$			p_y		
s_A	a_1	a_1'			

Components of the same species may be "mixed" to form the actual molecular orbitals. In doing so, however, we bear in mind the principle (see Part I) that when the HAH angle is 90° the s_A orbital must be kept separate from the other A orbitals. The a_1–a_1' bond orbital is thus built from an in-phase combination of $1s_1 + 1s_2 + 1s_3$ and p_z in the 90° molecule but of $1s_1 + 1s_2 + 1s_3$ and s_A in the planar molecule. Because of the change from p_z to s_A the orbital becomes more tightly bound as the HAH angle increases. The *ee*–*e'e'* bond orbitals are built from an in-phase combination of $\left.\begin{matrix}1s_1 - 1s_2 \\ 1s_1 + 1s_2 - 1s_3\end{matrix}\right\}$ and $\left.\begin{matrix}p_x \\ p_y\end{matrix}\right\}$ in both 90° and planar molecules. There is thus no hybridization-change in the contributing A valencies as the HAH angle changes. The orbitals however are antibonding between the H atoms and therefore by principle (iii) given in Part I become more tightly bound as the HAH angle increases. The a_1–a_1' orbital is built from an out-of-phase combination of $1s_1 + 1s_2 + 1s_3$ and p_z in the 90° molecule but (necessarily because of its symmetry) from $1s_1 + 1s_2 + 1s_3$ and s_A in the planar molecule. This orbital therefore becomes more tightly bound as the HAH angle increases; it is the analogue of the orbital which in AB_2 molecules causes the trihalide ions to have linear or nearly linear ground states. The $\bar{e}\bar{e}$–$\bar{e}'\bar{e}'$ orbitals are built from out-of-phase combinations of the $\left.\begin{matrix}1s_1 - 1s_2 \\ 1s_1 + 1s_2 - 1s_3\end{matrix}\right\}$ and $\left.\begin{matrix}p_x \\ p_y\end{matrix}\right\}$ components in both 90° and planar molecules. They are antibonding between the H atoms and therefore become more tightly bound the further the H atoms are apart. The a_1–a_2'' orbital represents a pure *s*-orbital of A in the 90° molecule and a pure p_z orbital of A in the planar molecule; it therefore becomes less and less tightly bound as the HAH angle increases.

Shapes of AH_3 *Molecules.*—Fig. 3 shows a qualitative correlation diagram between the orbitals of the pyramidal and the planar AH_3 molecules. The three lowest-energy curves all descend from left to right. One therefore expects AH_3 molecules containing six or less valency electrons to be planar. BH_3 and the carbonium ion CH_3^+ supply examples. Evidence exists that the ion CH_3^+ prefers a planar form (see Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184). On the other hand, a molecule such as NH_3 or OH_3^+, containing eight valency electrons, has to place two electrons in the a_1–a_2'' orbital whose curve in Fig. 3 rises steeply from left to right. It is to be expected, therefore, that the ammonia molecule should be pyramidal. The actual value of the HAH angle in AH_3 molecules containing eight valency electrons naturally varies somewhat with the nature of A. From NH_3 to PH_3 to AsH_3 to SbH_3 the angle decreases by some 15° (∠HNH = 106° 47′; Herzberg, "Infra-red and Raman Spectra," van Nostrand, New York, 1945: ∠HPH = 93° 50′, ∠HAsH = 91° 35′, ∠HSbH = 91° 30′; Nielsen, *J. Chem. Physics*, 1952, **20**, 759). The decrease could be plausibly attributed to a smaller drop from left to right of the *ee*–*e'e'* and a_1–a_1' curves as the size of atom A increases.

It has often been suggested that the CH_3 radical is planar. The radical has, however, seven valency electrons, one of which has to occupy the a_1–a_2'' orbital. According to Fig. 3, therefore (cf. NO_2), it is unlikely that the radical is planar in its ground state.* It should have a HCH angle intermediate between 120° and the HNH angle of the ground state of NH_3.

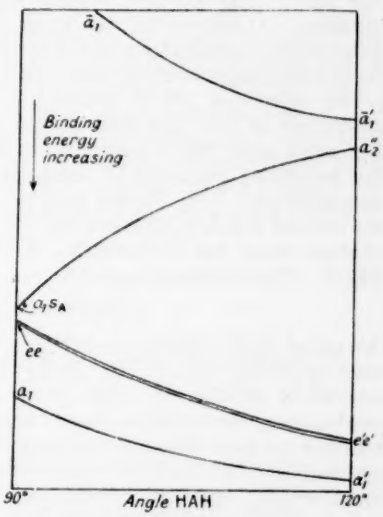
* Linnett and Poë (*Trans. Faraday Soc.*, 1951, **47**, 1033) have also arrived at the conclusion that the CH_3 radical is not planar.

However, even in NH_3 the potential barrier to inversion is not very high (2076 cm.$^{-1}$). In CH_3 this potential barrier should be considerably less. Inversion is likely to be so easy a process, therefore, that experiments to determine the presence or absence of optical activity in a product CRR'R''Y formed from an optically active compound CRR'R''X *via* a reaction involving the free radical CRR'R'' will not distinguish the planarity or otherwise of the radical.

When BH_3 forms the co-ordination complex OC $\longrightarrow$ BH_3, the electrons donated to the BH_3 enter the a_1–a_2'' orbital, so that the BH_3 group becomes pyramidal (Gordy, Ring, and Burg, *Phys. Review*, 1950, **78**, 512).

According to Fig. 3, AH_3 molecules containing 10 valency electrons should be planar or nearly planar. Unfortunately, no such molecules (*e.g.*, FH_3) are known to exist—a fact which is understandable in view of the anti-bonding properties of the $\bar{a}_1$–$\bar{a}_1'$ orbital which would have to be occupied in the ground state of a 10-electron molecule.

FIG. 3.



The fundamental reason for the pyramidal shape of an 8-electron molecule may be alternatively stated as follows (cf. Part II). In the ground state of such a molecule, two electrons have to occupy an orbital localized entirely on the central atom. These lone-pair electrons repel the electrons in the A–H bonds. If the molecule were planar they would be in a pure p_z orbital. As a result of the repulsion they move somewhat away from the bond electrons in the $+z$ direction (corresponding to hybridization of the s and the p_z valencies of A). Also as a result of the repulsion, the bond electrons move further away from atom A (corresponding to increasing p-character and consequent reduced electronegativity of the A valencies pointing towards the H atoms). When there are no lone-pair electrons on A the molecule is planar in its ground state. In the ground state of a 10-electron molecule a second lone pair of electrons would have to occupy the second orbital that can be built from s and p_z orbitals of A. A second hybrid orbital of this sort would point in the $-z$ direction and so cause the bond electrons to be subject to as much repulsion from above the molecular plane as from below.

The localization of the orbitals shown in Fig. 3 should be of help in interpreting the reactivity of AH_3 molecules. For example, the two most weakly bound electrons of NH_3 should be localized on the N atom. It is natural, therefore, that NH_3 reacts towards electrophilic reagents at the N atom.

Spectra of AH_3 *Molecules.*—Fig. 3 may be used to discuss the long-wave-length spectra of AH_3 molecules. The intra-valency-shell absorption transition of NH_3 of longest wave-length should be

$$(a_1)^2(e)^4(a_1)(\bar{a}_1),\ ^1A_1 \longleftarrow (a_1)^2(e)^4(a_1)^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (1)$$

The transition is analogous to the following transition of the N_2 molecule :

$$KK'(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u)^4(\sigma_g 2p)(\sigma_u 2p),\ ^1\Sigma_u^+ \longleftarrow KK'(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u)^4(\sigma_g 2p)^2,\ ^1\Sigma_g^+$$

$(\bar{a}_1)$ is anti-bonding between the H_3 group and N, just as $(\sigma_u 2p)$ is N$\longleftrightarrow$N anti-bonding. For the N_2 molecule the (π_g) orbital lies below the $(\sigma_u 2p)$ orbital. The (e) orbital corresponds to the (π_g) orbital, but because of its additional H$\longleftrightarrow$H anti-bonding character is expected to lie above $(\bar{a}_1)$. Transition (1) should lead to an increase of HNH angle (to a nearly planar form) and also of N–H distance. It is an allowed transition,

polarized parallel to the symmetry axis. The allowed nature means that only the totally symmetrical vibrations should occur in the upper state. In view of the expected change of both angle and distance, one would expect both the a_1 vibrations to be aroused. The frequencies of both these should be greatly lowered relatively to the ground state. In fact, because of the strongly anti-bonding nature of the upper ($\bar{a}_1$) orbital the transition may well give rise to continuous absorption. Experimentally, the first absorption region of ammonia occurs from 2167 to 1675 Å ($\lambda_{max.}$ at *ca.* 1900 Å). Thompson and Duncan (*J. Chem. Phys.*, 1946, **14**, 573) were unable to find an absorption system of longer wave-length, even in tubes 10 m. long with the gas at 1 atmosphere. The absorption consists of diffuse bands which, according to Duncan (*Phys. Review*, 1935, **47**, 822) belong to a single v' progression. The upper state frequency is 878 cm.$^{-1}$. Dixon (*ibid.*, 1933, **43**, 711) had earlier classified the bands with the aid of two upper-state frequencies, *viz.*, 890 and 2720 cm.$^{-1}$. The intensity is such that there is little doubt of the allowed nature of the transition. It follows that the upper-state frequency or frequencies represent one or both of the two a_1, parallel frequencies (*ca.* 950 and 3334 cm.$^{-1}$ in the ground state). The slow rise to a maximum intensity shows that the dimensions of the molecule change considerably in the excitation. It is possible, therefore, that the observed absorption could be interpreted as (1). The high energy of the excitation (origin 46,157 $\pm$ 30 cm.$^{-1}$), however, must mean that it cannot lie far from the Rydberg transition of longest wave-length. The ionization potential of ammonia is known to lie quite low. From unpublished electron-impact data, Sugden finds a value 10·8 v. The region 2178—1675 Å may therefore contain the first Rydberg transition of the molecule. For comparison, one may cite ethylene which has an ionization potential of 10·50 v and a first Rydberg transition at 1744 Å. This Rydberg transition may be formulated as:

$$(a_1)^2(e)^4(a_1)(a_1 3s),\ ^1A_1 \longleftarrow (a_1)^2(e)^4(a_1)^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (2)$$

The upper orbital closely resembles a 3*s* orbital of the N atom and the transition is of the same symmetry type as (1). It should cause an increase of HNH angle (because of the removal of an electron from the a_1–a_2'' orbital). Since, however, the upper orbital is non-bonding, the transition should not cause much change of NH length. In other words, it should not have the same tendency as (1) to lead to dissociation of the molecule. It is possible, therefore, that the observed bands in the first absorption region of NH_3 are due to transition (2); but that they are complicated by the presence of transition (1) in the same region. Such an interpretation has the advantage that, if the upper orbital of (1) is repulsive, we could explain the observed diffuseness of the bands by supposing predissociation to occur in the upper state of (2). Photochemical work provides strong evidence that dissociation to NH_2 and H occurs in the absorption. The interpretation would be exactly analogous to that given by us for the first absorption region of the H_2O molecule (Part I, p. 2263). Mulliken (*J. Chem. Phys.*, 1933, **1**, 492; 1935, **3**, 506) has earlier ascribed the 2167—1675-Å system to transition (2). The probability that two transitions are concerned in the system complicates comparison of observed and calculated transition intensities (Thompson and Duncan, *loc. cit.*). Transition (2) might arouse strongly only the $\nu_2(a_1)$ frequency (950 cm.$^{-1}$ in the ground state) and not the $\nu_1(a_1)$ vibration (3334 cm.$^{-1}$ in the ground state), in possible agreement with Duncan's vibrational analysis.

That the first absorption system of NH_3 does cause a change of HNH angle is supported by the appearance of the NH bending vibration in the corresponding absorption region of methylamine (Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75). The banded absorption of this amine lies between 2500 and 2000 Å and gradually passes into a continuum at shorter wave-lengths.

The first absorption of the PH_3 molecule consists of two or three diffuse bands between 2300 and 2200 Å, followed by continuous absorption from 2200 to beyond 1850 Å (Melville, *Nature*, 1932, **129**, 546; Cheesman and Emeléus, *J.*, 1932, 2847). We suggest that the continuous absorption belongs to transition (1) and the bands to transition (2) [$(a_1 4s)$ replacing $(a_1 3s)$] perturbed by transition (1). The first absorption of AsH_3 and SbH_3 (Cheesman and Emeléus, *loc. cit.*) is continuous and may be ascribed to transition (1), perhaps involving also the appropriate analogue of (2).

The two lowest-energy intra-valency-shell absorption transitions of the CH_3 radical should be

$$\ldots (a_1'), {}^2A_1'' \longleftarrow \ldots (a_1''), {}^2A_1'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\ldots (e')^3(a_1'')^2, {}^2E' \longleftarrow \ldots (e')^4(a_1''), {}^2A_1'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Both are allowed transitions. Which would be the lower in energy is uncertain. By analogy with NH_3, it is probable that the absorption corresponding to (3) would lie at wave-lengths shorter than 2500 Å. If absorption due to the CH_3 radical is found at wave-lengths above 2500 Å it is probably to be interpreted as (4). Transition (4), however, is likely to be weak, since it corresponds to one that would be forbidden if the radical were planar; and the departure from planarity may not be great. Since the ionization potential of the CH_3 radical is known to be only *ca.* 10·0 v, it is probable that (3) would lie close to the transition

$$\ldots (3sa_1'), {}^2A_1'' \longleftarrow \ldots (a_1''), {}^2A_1'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Transitions (3) and (5) are polarized along the symmetry axis, *i.e.*, along the axis of least moment of inertia. The molecule is a symmetric top and the transitions should give rise to parallel bands. Both should cause an increase of HCH angle. The upper state of both would probably be planar. Transition (3) should cause a big increase of C–H distance. The strongly anti-bonding nature of the upper (a_1'') orbital may cause (3) to give rise to continuous absorption. Transition (4) should give rise to perpendicular bands. It should result in a marked decrease of apex angle and an increase of C–H distance. No electronic spectrum of CH_3 is yet known, but these detailed predictions should help in the search now being undertaken in various laboratories for that spectrum.

LEEDS UNIVERSITY. [*Received, May 15th,* 1953.]

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470. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part V.* Tetratomic, Non-hydride Molecules,* AB_3.

By A. D. WALSH.

The procedure developed in previous papers of this series is applied to tetratomic, non-hydride molecules, AB_3. A correlation diagram is plotted between the orbitals possible for planar AB_3 molecules and those possible for pyramidal molecules. This enables a discussion to be given of the shapes of such molecules, and comments to be made on their reactivities and spectra. AB_3 molecules containing $\geqslant 24$ valency electrons are planar in their ground states. Molecules containing 25 or 26 valency electrons should be pyramidal in their ground states, the BAB angle decreasing with increase in the number of electrons. Molecules containing 24 valency electrons should be pyramidal in their first excited states. The ground states of molecules containing 28 valency electrons should be planar or nearly planar.

Orbitals of Non-hydride, AB_3 *Molecules.*—The lowest-lying possible orbitals for a planar AB_3 molecule may be approximately described as follows. (i) Three *s* lone-pair orbitals, one on each of the B atoms. In known AB_3 molecules, B is usually of high electronegativity, greater than that of A. To a first approximation, therefore, these *s* orbitals may be supposed so tightly bound that they hardly interact with each other or with other orbitals. They remain essentially atomic in character and vary little in binding energy as the BAB angle is varied. (ii) Three bonding orbitals. Regarded as localized orbitals, they are formed from sp^2 hybrid valencies of A overlapping in-phase with *p* valencies of the B atoms that point towards atom A. Regarded as non-localized orbitals, they are of species a_1', e', e', as described for AH_3 molecules. (iii) Three orbitals which are approximately *p* lone-pair orbitals, one on each of the B atoms. The axis of each of these *p* orbitals lies in the molecular plane and perpendicular to the adjacent B–A line. The orbitals are approximately non-bonding because the B atoms are far apart. They form

* Part IV, preceding paper.

non-localized orbitals as indicated in Fig. 1. Two of the orbitals are degenerate and of species e'. They have a net slight bonding effect between the B atoms. The third orbital is of species a_2' and is slightly anti-bonding in each B–B distance; it therefore is of slightly higher energy than the e' orbitals. (iv) Four orbitals built from p orbitals, on the A and the three B atoms, which have their axes perpendicular to the molecular plane (see Fig. 2). The lowest-energy orbital of these has all four p orbitals overlapping in-phase. It is of species a_2'' and is bonding in each A–B and B–B distance. The next two orbitals each have a nodal plane perpendicular to the molecular plane and passing through atom A. They are degenerate, the two-fold degeneracy arising from the two independent and mutually perpendicular possible settings of the above nodal plane. Their species symbol is thus e''. They have a net anti-bonding effect between the B atoms and are A$\leftrightarrow$B non-bonding. The fourth orbital has the p orbital on atom A overlapping out-of-phase with each of the p orbitals on the B atoms. It is of species a_2'' and is anti-bonding in each A–B distance but bonding between the three B atoms. To denote its A$\leftrightarrow$B anti-bonding character it is written $\bar{a}_2''$. The fact that B usually has a higher electronegativity than A means that the first three orbitals are more localized on the B atoms than on A, while the fourth orbital is more localized on atom A. The argument is the same as that used in Part II in the discussion of the localization of orbitals. The bonding or anti-bonding properties of the orbitals in (iii) and (iv) suggest that the order of decreasing binding energy is $a_2''e'e'e''e''a_2'$, followed by $\bar{a}_2''$. (v) Three orbitals which are built by

FIG. 1. (*The choice of form for the* e′ *orbitals is not unique.*)

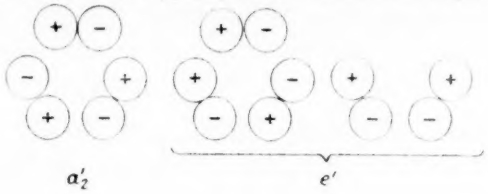
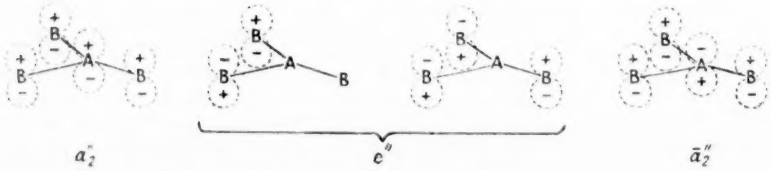


FIG. 2. (*The forms of the* e″ *orbitals are not unique.*)



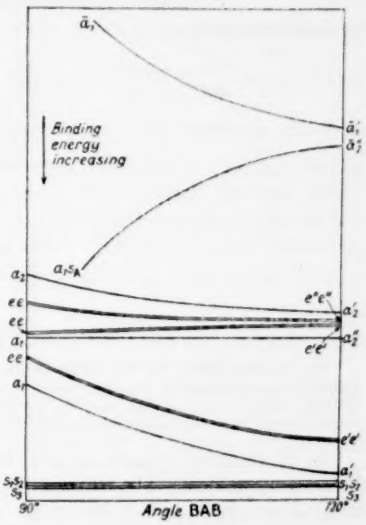
the out-of-phase overlap of an orbital on A with an appropriate group orbital compounded from the three B p orbitals whose axes lie along the A–B lines. In the lowest of these (species a_1') the three B p orbitals overlap in-phase with each other but out-of-phase with a central s orbital on A. The orbital is anti-bonding in each A–B distance and is therefore written $\bar{a}_1'$. It corresponds to the $\bar{a}_1'$ orbital described for AH_3 molecules, and is more localized on A than on the B atoms.

The $\bar{a}_2''$ orbital corresponds to the a_2'' orbital described for AH_3 molecules. Whereas the latter was non-bonding, however, the former is anti-bonding. In AH_3 molecules the a_2'' undoubtedly lies well below the $\bar{a}_1'$ orbital. In non-hydride AB_3 molecules the anti-bonding character of $\bar{a}_2''$ causes it to become of higher energy relative to the other orbitals. It is therefore uncertain in AB_3 whether $\bar{a}_2''$ or $\bar{a}_1'$ lies the higher. The point is exactly analogous to the question whether $\bar{\pi}_u$ or $\bar{\sigma}_g$ lies the lower for a linear AB_2 molecule (Part II).

The lowest-lying orbitals for a pyramidal AB_3 molecule in which the BAB angle is 90° may be approximately described as follows. (i) Three s lone-pair orbitals, one on each B atom. These remain essentially atomic in character and vary little in binding energy as the BAB angle is varied. In Fig. 3, which correlates the orbitals of pyramidal and planar

AB_3 molecules,* they are therefore represented by three horizontal lines close together. (ii) Three bonding orbitals. Regarded as localized orbitals, these utilize pure p valencies of A. Regarded as non-localized orbitals, they are of species a_1, e, e and are represented by lines that fall from left to right in Fig. 3, as described for AH_3 molecules. (iii) Six approximate lone-pair p orbitals, two on each B atom and each of axis perpendicular to the adjacent A–B line. Since these orbitals are approximate lone-pair orbitals they are represented in Fig. 3 by lines that remain fairly close together whatever the angle BAB. Moreover, as the angle changes, they involve no changing hybridization of A valencies. Whether they increase or decrease in binding energy as the BAB angle increases is therefore determined by whether they are B⟷B anti-bonding or bonding respectively [principle (iii) of Part I]. These p orbitals may be separated into two groups; those whose axes lie in the plane of the three B atoms and those whose axes do not. Consider the former first. The non-localized combinations of the lone-pair orbitals are of species e, e, a_2, corresponding to the e', e', a_2' group of the planar molecule. The e, e orbitals are weakly bonding between the B atoms as a net effect. They therefore are more tightly bound when the B atoms are close together (angle BAB = 90°) than when far apart (angle BAB = 120°), and are represented in Fig. 3 by lines that rise from left to right. The a_2 orbital is anti-bonding between the B atoms. It is therefore more tightly bound in the planar molecule and is represented by a line that falls from left to right.

FIG. 3.



Considering now the remaining three B p orbitals: these give rise to a_1, e, e orbitals corresponding to the a_2'', e'', e'' group of the planar molecule. The e, e or e'', e'' orbitals have a net anti-bonding effect between the B atoms. They are therefore represented in Fig. 3 by lines that fall from left to right. The a_1 or a_2'' orbital is bonding between the B atoms and might therefore be expected to rise from left to right in Fig. 3. On the other hand, it probably changes from being built almost solely from B orbitals in the 90° molecule to being built increasingly also from an A p orbital as the BAB angle increases, *i.e.*, it increases in A⟷B bonding character. As a result, the orbital may vary comparatively little with change of angle and has been represented in the Figure by a horizontal line. In any case, however, the variation in the a_2'', e'', e'' or a_2', e', e' group will be small compared with the variation in the a_1', e', e' group. (iv) An orbital that is approximately an s orbital on atom A. It is of species a_1 (written a_1s). As the BAB angle increases, this orbital rises steeply in energy, as in AH_3, because it becomes more and more built from a p orbital of A. In AB_3, in addition, it becomes more and more A⟷B anti-bonding, tending to approach the $\bar{a}_2''$ orbital of the planar molecule. (v) An orbital of species a_1 (written $\bar{a}_1$) which is anti-bonding in each A–B distance and corresponds to the $\bar{a}_1'$ orbital of the planar molecule. It is built from an s orbital of A in the planar molecule, but from a p_z orbital of A in the 90° molecule and is therefore represented in Fig. 3 by a curve that falls steeply from left to right. If $\bar{a}_1'$ for the planar molecule lies below $\bar{a}_2''$, the steep curve from the a_1s orbital will lead eventually to $\bar{a}_1'$. Otherwise, curves of the same species would cross. Similarly, the curve from the $\bar{a}_1'$ orbital would then lead not to the $\bar{a}_1'$ but to the $\bar{a}_2''$ orbital.

Shapes of AB_3 *Molecules.*—Of the twelve lowest orbital curves in Fig. 3, all but two either fall from left to right or remain roughly constant in energy. The two that rise only

* For clarity, Fig. 3 (like Fig. 1 of Part IV) is over-simplified. Thus the a_1s_A and ee bonding orbital curves probably cross (see Part VII). Crossings (or avoided crossings) would complicate the diagram, but need not upset the basic ideas of this paper.

do so slightly. One therefore has a strong expectation that AB_3 molecules containing 24 or less valency electrons will be planar. This is borne out by the facts (see Table). A molecule with 25 or 26 valency electrons, however, has to have one or two electrons, respectively, in the a_1s–$\bar{a}_2''$ or $\bar{a}_1'$ orbital. This means that such molecules can be expected to be pyramidal, the BAB angle being less for a 26- than for a 25-electron molecule. There appears to be only one example of a 25-electron molecule, *viz.*, ClO_3 which, although probably pyramidal, has an unknown OClO angle. 26-Electron molecules are all pyramidal as expected, the BAB angle being ~100°. As with triatomic molecules, one notices the importance of pure number in determining the shape of a molecule. The Table includes a few B_2AC molecules because a correlation diagram very similar to Fig. 3 (except that no orbitals are now degenerate) should apply to such molecules (see following papers). The linkage of shape with number of valency electrons should therefore be the same for B_2AC as for AB_3 molecules.

Shapes of tetratomic AB_3 (*and some* B_2AC) *molecules.*

No. of valency electrons	Molecule				Shape
24	CO_3^{--}		NO_3^-		Planar
	SO_3		NO_2Cl		
	BF_3		BO_3^{3-}		
	BCl_3		InI_3		
	BBr_3		$GaCl_3$		
	$COCl_2$		$GaBr_3$		
	$COBr_2$		$CSCl_2$		
25	ClO_3				Pyramidal
26	IO_3^-	PF_3	104°	SbI_3	~99°
	ClO_3^-	PCl_3	100° 6′	$BiCl_3$	~100°
		PBr_3	101°	$BiBr_3$	100°
		PI_3	100°	$SOCl_2$: ∠ClSCl	114°
		$AsBr_3$	100°	∠ClSO	106°
		AsI_3	100°	$SOBr_2$: ∠BrSBr	96°
		$AsCl_3$	98° 25′	NF_3 : 102° 9′	

The values given are the BAB angles where known. Except for NF_3, PCl_3, and $AsCl_3$, they are quoted from Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46. The value for NF_3 comes from a micro-wave determination by Sheridan and Gordy (*Phys. Review*, 1950, **79**, 513). The values for PCl_3 and $AsCl_3$ come from micro-wave determinations by Kisliuk and Townes (*J. Chem. Phys.*, 1950, **18**, 1109).

The 22-electron hypothetical molecule CO_3 should be planar and paramagnetic. The 23-electron molecule NO_3 (Sidgwick, "The Chemical Elements and their Compounds," Oxford Univ. Press, 1950, Vol. I, pp. 691—692) should also be planar.

One deduces from Fig. 3 that the first excited state of CO_3^{--}, NO_3^-, BF_3, or SO_3 should be pyramidal in its equilibrium form. Relatively to, say, ClO_3 the first excited states of these molecules have one less electron stabilizing the planar form. If ClO_3 is pyramidal, therefore, these excited states should certainly be so. Similarly, when BF_3 forms the co-ordination complex $(CH_3)_2O \rightarrow BF_3$, the electrons donated to the BF_3 have to enter the a_1s–$\bar{a}_2''$ or $\bar{a}_1'$ orbital, resulting in the BF_3 group becoming pyramidal (see Dunderman and Bauer, *J. Phys. Chem.*, 1946, **50**, 32).

According to Fig. 3, 28-electron molecules should be planar or nearly so. Unfortunately a structure determination has been reported for only one 28-electron molecule, *viz.*, ClF_3, namely, by Allen and Sutton (*loc. cit.*) as a personal communication from Wahrhaftig, so that the evidence for it cannot be critically examined. According to it, ClF_3 is a pyramidal molecule with the ClFCl angle 86·5° ± 1·5°. This is not in accord with expectations from this paper and further evidence is awaited. If it should prove that the molecule is after all far from planar, it must mean that not all the premises upon which the present prediction of near planarity are based apply to ClF_3. The present discussion is confined, for example, to molecules wherein only *s* and *p* atomic orbitals are used, and assumes that the only possible shapes belong to the D_{3h} or the C_{3v} symmetry class.*

* *Added in Proof.*—ClF_3 has now been reported to be planar (Burbank and Bensey, *J. Chem. Phys.*, 1953, **21**, 602; Smith, *ibid.*, p. 609), in agreement with our expectations. However, it is reported as a slightly distorted T-shaped molecule; this could not have been predicted by our work, which was limited to a consideration of the symmetrical C_{3v} and D_{3h} models only.

Reactivity of AB_3 *Molecules.*—Fig. 3 also enables one to discuss the reactivities of tetratomic molecules. A radical such as NO_3, for example, should have its odd electron in an e'' orbital which, we have argued, is largely localized on the O atoms. We have already seen (Part II) that the odd electron of the NO_2 molecule is localized largely on the N atom. One would expect therefore the structure of N_2O_5 (which is probably formed from $NO_3 + NO_2$) in the gas phase to be $O_2N{\cdot}O{\cdot}NO_2$ rather than $O_2N{\cdot}NO_3$. This is known to be correct (Sidgwick, *op. cit.*).* Similarly, one expects the N_2O_6 molecule to be $O_2N{\cdot}O{\cdot}O{\cdot}NO_2$ rather than the ethane-like structure $O_2N{\cdot}NO_4$. This again appears to be true (Sidgwick, *op. cit.*). The odd electron of the NO molecule lies in an orbital more localized on the N than on the O atom (cf. Part II). It follows that the N_2O_3 molecule is expected to have the structure $O{\cdot}N{\cdot}NO_2$. Similarly, N_2O_4 (which dissociates to $2NO_2$ rather than to $NO + NO_3$) should have the structure $O_2N{\cdot}NO_2$ rather than $O{\cdot}N{\cdot}O{\cdot}NO_2$ or $O{\cdot}N{\cdot}O{\cdot}O{\cdot}N{\cdot}O$. Pauling suggested the second of these because the first violated his "adjacent charge" rule. However, there is now little doubt that the first is correct (Ingold and Ingold, *Nature*, **1947**, **159**, 743; Walsh, *J. Chem. Phys.*, **1947**, **15**, 688). Sidgwick (*op. cit.*) gives the structure ONONO for the N_2O_3 molecule, but the evidence for this does not appear unambiguous. NO should react with NO_3 to give the molecule $O{\cdot}N{\cdot}O{\cdot}NO_2$ which could give $2NO_2$. The step $NO + NO_3 = 2NO_2$ may occur in the reaction between NO and O_2 to give (finally) NO_2.

Similar considerations should govern the interaction of PO, PO_2, and PO_3 radicals, and are relevant to an understanding of how P_4 on oxidation produces P_4O_{10} molecules.

Spectra of AB_3 *Molecules.*—By the Franck–Condon Principle, since the first excited states of such molecules as CO_3^{--}, NO_3^-, BF_3, or SO_3 should be non-planar, one expects the longest-wave-length electronic transitions of these molecules to occupy a wide region of the spectrum. This is true of, *e.g.*, SO_3, which has a long-wave-length transition extending from 3000 to beyond 2200 Å. A further reason lies in the increase of A–B length that will occur in the transition. The $\bar{a}_2''$ and the $\bar{a}_1'$ orbital are both so highly A$\leftrightarrow$B anti-bonding that it is not surprising that all the known spectra of 26-electron molecules are continuous. The spectra of PCl_3, PBr_3, $AsCl_3$, $SbCl_3$, and $BiCl_3$ (Sponer and Teller, *Rev. Mod. Phys.*, **1941**, **13**, 75) supply examples.

The SO_3 absorption referred to above consists of weak, diffuse, bands superimposed on a continuous background. We suggest that the bands and the continuous background are to be interpreted as due to two transitions which may both be formulated

$$\cdots(a_2)(a_1),\ {}^1A_2 \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \quad . \quad . \quad . \quad . \quad . \quad (1)$$

corresponding to the two transitions

$$\cdots(a_2')(\bar{a}_2''),\ {}^1A_1'' \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$\cdots(a_2')(\bar{a}_1'),\ {}^1A_2' \longleftarrow \cdots(a_2')^2,\ {}^1A_1' \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Both (2) and (3) are forbidden; (2) should lead to a pyramidal and (3) to a planar upper state. In agreement the absorption is not very strong, ε slowly increasing from a very low value at 3000 Å to about 100 at 2150 Å (Fajans and Goodeve, *Trans. Faraday Soc.*, 1936, **32**, 511). It should be noted, however, that the peak of the absorption lies at some unknown wave-length below 2150 Å. The banded part of the absorption appears to begin at about 2700 Å, but the bands have only been measured below 2500 Å. They are separated by an approximately constant frequency difference of

* In the solid state, N_2O_5 is known to be NO_2^+,NO_3^- (Grison, Eriks, and de Vries, *Acta Cryst.*, **1950**, **3**, 290).

430 cm.$^{-1}$. The probable interpretation of this is that it represents either the symmetrical stretching or the symmetrical bending vibration (both of species a_1 for a pyramidal upper state, or a_1' and a_2'' respectively for a planar form) of the upper state. In the ground state the a_1'- and the a_2''-vibration have frequencies of 1069 and 653 cm.$^{-1}$ respectively (Gerding and Lecomte, *Physica*, 1939, **6**, 737). The bands have a curious flat-topped structure (see Figure given by Fajans and Goodeve, *loc. cit.*). Indeed, 430 cm.$^{-1}$ really refers to the measured separations of the minima (which alone are sharp) between the bands. No explanation of this band shape has yet been given.

The 23-electron NO_3 molecule is known to give rise to absorption bands between 7100 and 5000 Å (see Jones and Wulf, *J. Chem. Phys.*, 1937, **5**, 873). The extinction coefficient is quite high (~2000 at $\lambda_{max.}$ which is ~6650 Å). This suggests the identification (see Fig. 3)

$$\cdots(e')^3(a_2')^2,\ {}^1E' \longleftarrow \cdots(e')^4(a_2'),\ {}^1A_2' \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now (4) is an allowed transition, the molecule being planar in the equilibrium forms of both combining states. Not surprisingly, therefore, the bands are quite different from those of SO_3, being comparatively sharp and narrow. Moreover, the very long wave-length of this NO_3 absorption system is in accord with the discussion above and with the closeness of the binding energies of the orbitals a_2'', e'', e'' and e', e', a_2' in Fig. 3. If (4) is assumed to be correct, the bands should turn out under higher dispersion to be perpendicular in type. Since the (e') and (a_2') orbitals concerned are respectively O←→O bonding and anti-bonding, the main vibrational frequency involved should be the a_1' totally symmetrical stretching vibration of the upper state.

The absorption shown by dilute aqueous solutions of nitrates (a rounded peak between 3000 and 2500 Å with $\varepsilon \sim 7$; Sponer and Teller, *loc. cit.*; Katzin, *J. Chem. Phys.*, 1950, **18**, 789) is probably to be interpreted as transition (1) of the nitrate ion, more or less perturbed by the adjacent solvent and cations.

LEEDS UNIVERSITY. [*Received, May 15th*, 1952.]

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471. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VI.** H_2AB *Molecules.*

By A. D. WALSH.

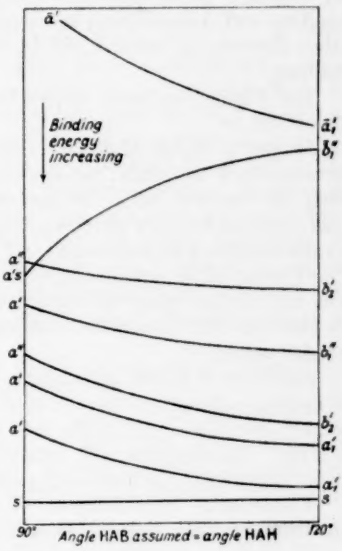
The correlation diagram between the orbitals possible for planar and non-planar H_2AB molecules is obtained as a special case of the diagram given in Part V for AB_3 molecules. The diagram is used to interpret the shapes of H_2AB molecules and especially to discuss the near ultra-violet spectrum of formaldehyde. It is shown that the first excited state of formaldehyde should be non-planar, though possibly only slightly so. Confirmatory evidence is found in the fluorescence spectrum. Various interpretations of the near ultra-violet spectrum are discussed, without it being possible to reach a final decision. There are, however, strong arguments for the occurrence of ν_5 in the spectrum; occurrence of this may be regarded as due to the O atom in the upper state lying very slightly out of the mirror plane which bisects the HCH angle.

PLANAR C_2AB molecules belong to the symmetry class C_{2v}. The symbols appropriate to their orbitals have been defined in Part I of this series of papers. The only symmetry element present in non-planar C_2AB molecules is the reflection plane that contains the A–B bond and bisects the CAC angle. Such molecules belong to the C_s symmetry class. For them the only orbital symbols to be used are a' and a'' according as an orbital is symmetrical or anti-symmetrical, respectively, with respect to reflection in the only plane of symmetry. The present paper deals with H_2AB molecules, leaving the non-hydride C_2AB molecules for a following paper.

Orbitals of H_2AB *Molecules.*—For H_2AB molecules the Figure shown in Part V reduces to that below. There is now only one low-lying *s* lone-pair orbital on the peripheral atoms,

* Part V, preceding paper.

namely, that on atom B. As before we assume this to take no part in the bonding, whatever the angle HAH or HAB. For simplicity we shall assume angle HAH to be equal to angle HAB. This is unlikely always to be true (cf. $SOCl_2$ in the Table of Part V), but the assumption enables us to plot the binding energy as a function of one instead of two quantities and will not invalidate any of the conclusions reached in this paper. The lowered symmetry of H_2AB relative to AB_3 means that the degeneracy present in several pairs of orbitals of AB_3 is removed in H_2AB. Thus the three main bonding orbitals are now all separate. One of them will be localized largely in the A–B bond. In formaldehyde, CH_2O, judged from the electronegativities of the O(2*p*) and H(1*s*) orbitals (see, *e.g.*, Walsh, *Proc. Roy. Soc.*, 1951, *A*, **207**, 13) this orbital will be the most tightly bound of the three. The appropriate label for this orbital will be a_1 for C_{2v} symmetry (or a_1' if we symbolize its symmetrical nature with respect to reflection in the molecular plane) and a' for C_s symmetry. The other two main bonding orbitals are largely localized in the H_2A group. One of them corresponds to the in-phase and the other to the out-of-phase overlap of the two AH bond orbitals with each other. The C_{2v} symbols are respectively a_1 and b_2; and the C_s symbols a' and a''. The three bonding orbitals increase in binding energy from left to right in the Figure because they are built from A *p* orbitals on the left but A sp^2 orbitals on the right. The a_2'', e'', e'' group of AB_3 orbitals is now represented by a single orbital localized in the A–B bond. Generally speaking, it is more localized on B than on A. In the planar molecule this orbital is "π" with respect to the local symmetry, and b_1 with respect to the C_{2v} symmetry. In the non-planar molecule it is labelled a'. In the planar molecule the orbital is built from a *p* orbital on atom A overlapping in-phase with a *p* orbital on atom B. When angle HAH = angle HAB = 90°, however, the three *p* orbitals of the A atom are taken up in forming the three main bonding orbitals. The b_1 orbital therefore becomes more and more A⟷B bonding as the angles increase. The curve representing the orbital has consequently been drawn to drop from left to right. The corresponding orbital for AB_3 was B⟷B bonding, which offset to some extent this tendency to become more tightly bound in the planar molecule. No such offsetting factor is present for the H_2AB molecule. The e', e', a_2' group of AB_3 orbitals is now represented by a single lone-pair orbital largely localized on the B atom. In the planar molecule the axis of this orbital lies of course in the molecular plane. The C_{2v} symbol is b_2. The C_s symbol is a''. The orbital is largely non-bonding and must therefore be represented by a curve that is not far from horizontal. To some extent, however, the orbital must interact with the a''–b_2 AH_2 group orbital. This interaction increases the binding energy of the latter orbital and decreases that of the former. The interaction will obviously be the greater the nearer the AH_2 group is to the C atom. It follows that the upper a''–b_2' orbital will descend to some extent from left to right. In other words, the reason is that the upper a''–b_2' orbital is somewhat AH_2⟷C anti-bonding. Considering the non-bonding or anti-bonding nature of the a''–b_2' orbital compared with the bonding nature of the a'–b_1'' orbital, we see that the former is likely to be the more weakly bound. The steep a_1s–$\bar{a}_2''$ curve of the AB_3 correlation diagram has an analogue labelled $a's$–$\bar{b}_1''$ in the H_2AB diagram. It is more localized on the A than on the B atom. In the non-planar H_2AB molecule it is largely an A *s* orbital. In the planar molecule it becomes built from a *p* orbital on atom A overlapping out-of-phase with a B *p* orbital. Both these *p* orbitals have their axes at 90° to the molecular plane. In the planar molecule the molecular orbital is thus A⟷B anti-bonding. The orbital decreases greatly in binding energy



from left to right in the Figure, partly because it becomes built from A p rather than from A s, and partly because it becomes A←→B anti-bonding instead of non-bonding.

The $\bar{a}_1$–$\bar{a}_1'$ curve of the AB_3 diagram also has its analogue, now labelled $\bar{a}'$–$\bar{a}_1'$, in the H_2AB diagram. Three anti-bonding orbitals, symmetric with respect to reflection in the molecular plane, are possible. These will be labelled $\bar{a}_1'$, $\bar{a}_1'$, and $\bar{b}_2'$ corresponding to the three bonding orbitals a_1', a_1', and b_2' of the planar molecule. Two of these orbitals ($\bar{a}_1'$ and $\bar{b}_2'$) will be more localized in the AH_2 than in the AB group; $\bar{a}_1'$ will be H←→H bonding and A←→H anti-bonding, $\bar{b}_2'$ will be H←→H and A←→H anti-bonding. The other (lowest) $\bar{a}_1'$ orbital will be largely localized in the AB group, being A←→B anti-bonding.

The Figure has been drawn on the assumption that $\bar{b}_1''$ lies lower than the lowest $\bar{a}_1'$-orbital.

Shapes of H_2AB *Molecules.*—It is clear from the Figure that the ground state of the formaldehyde molecule, possessing 12 valency electrons, should be planar, in agreement with the known fact. On the other hand, the ground state of the H_2NF molecule, containing 14 valency electrons, will have two electrons in the $a's$–$\bar{b}_1''$ orbital; the molecule should therefore be non-planar. The ground state of the molecule H_2BF should be planar. The hypothetical radicals H_2NO and H_2CF should be non-planar in their ground states. The first excited state of formaldehyde is also expected to be non-planar, since it has lost an electron from an orbital stabilizing the planar form and has gained an electron in the $a's$–$\bar{b}_1''$ orbital.

Reactivity of H_2AB *Molecules.*—The Figure may be used in discussion of the reactivities of molecules in either their ground or their excited states. As a single example, the most weakly bound electron in the first excited state of CH_2O should be mostly localized on the C atom. If, therefore, the excited CH_2O molecule reacts with, *e.g.*, a H atom one would expect it to form the methoxyl radical.

Spectrum of Formaldehyde.—According to our Figure the lowest electronic states of the formaldehyde molecule should be

$$\cdots (b_2')^2,\ {}^1A_1 \text{ (the ground state)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\cdots (b_2')(\bar{b}_1''),\ {}^3A_2 \text{ or } {}^1A_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\cdots (\bar{b}_1'')^2,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

A two-electron jump would be necessary to reach state (3) by absorption from the ground state. These four states correspond to the known low-lying states of the O_2 molecule. The latter states, in order of increasing energy, are ${}^3\Sigma_g^-$ (the ground state), ${}^1\Delta_g$ (two-fold degenerate), and ${}^1\Sigma_g^+$. If protons are pulled out of one of the O nuclei to form CH_2O, ${}^3\Sigma_g^-$ becomes ${}^3A_2$; ${}^1\Delta_g$ becomes ${}^1A_1$ and ${}^1A_2$; and ${}^1\Sigma_g^+$ becomes ${}^1A_1$. A correlation diagram between the states of O_2 and of CH_2O therefore makes it clear (since curves of the same species cannot cross) that the ground state of CH_2O correlates with one of the components of the ${}^1\Delta_g$ state of O_2, while state (3) above correlates with the ${}^1\Sigma_g^+$ state of O_2.

Also according to the Figure, the lowest-energy absorption electronic transition of formaldehyde should be

$$\cdots (b_2')(\bar{b}_1''),\ {}^3A_2 \text{ or } {}^1A_2 \longleftarrow \cdots (b_2')^2,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad (4)$$

Mulliken (*J. Chem. Phys.*, **1935**, **3**, **564**) and McMurry and Mulliken (*Proc. Nat. Acad. Sci.*, **1940**, **26**, **312**) have previously arrived at the conclusion that ${}^1A_2 \longleftarrow {}^1A_1$ represents the lowest-energy singlet←singlet transition. They believe the near ultra-violet absorption of formaldehyde represents this singlet←singlet transition. Burawoy (*Discuss. Faraday Soc.*, **1950**, **9**, **70**) believes the absorption to represent a triplet←singlet transition.*

* Burawoy objects to the orbitals formulated in (4) being regarded as concerned in the transition. His evidence is not conclusive. For example, he takes as evidence against (4) the fact that a short-wave-length shift of the absorption takes place when the polarity of the double bond is increased. This, however, could easily be qualitatively explained in terms of (4). Consider the change from formaldehyde to acetone. Substitution of methyl groups will affect primarily the C atom of the CO group, and will reduce the binding energy of orbitals on that atom. Since therefore the upper orbital of (4) is largely on the C atom, a reason exists for a short-wave-length shift of the spectrum in acetone.

The transitions (4) are largely localized in the CO group, being from an orbital largely non-bonding and on the O atom to one that is rather more on the C than on the O and is C←→O anti-bonding. It is understandable therefore that, if one of the transitions (4) represents the near-ultra-violet absorption, this absorption in many carbonyl compounds should be very similar.

What has not been previously pointed out is that the upper states of the transitions (4) should be non-planar. One might, therefore, more properly write (4) as

$$\cdots(a'')(a's),\ ^3A'' \text{ or } ^1A'' \longleftarrow \cdots(b_2')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (5)$$

the upper states in their equilibrium forms having C_s rather than C_{2v} symmetry. However, the departure from planarity may be sufficiently small for the formulation (4) to be meaningful. This is especially likely when one remembers that even in NH_2F the inter-bond angle is probably ~107° (as in NH_3) and therefore that the inter-bond angle in the first excited state of formaldehyde (containing only one electron instead of two in the $a's$–b_1'' orbital) is unlikely to be less than about 113°, *i.e.*, the upper state is likely to be bent by only a few degrees from planarity. None the less, a slight departure from planarity in the upper state leads to the expectation that, in either absorption or fluorescence, progressions in the out-of-plane bending vibration ($\nu_6 b_1$ *) should appear in the system. Transitions (4) should also cause a marked lengthening of the CO bond. In addition to ν_6 one therefore expects the CO valency vibration ($\nu_2 a_1$) to appear both in absorption and in fluorescence.

In contrast to the upper states (2), the upper state (3) should be *strongly* bent. The bending tends to make (3) lie lower than would otherwise be the case.

In the light of these expectations let us now consider the formaldehyde spectrum.

Fluorescence Spectrum of Formaldehyde.—The fluorescence spectrum of formaldehyde has been studied by Brand (*J. Chem. Phys.*, 1951, **19**, 377), who succeeded in assigning quantum numbers to the vibrational bands such that the frequencies of those bands could be expressed by the formula

$$\nu = (28312{\cdot}7 - 113{\cdot}2p) + [(1191{\cdot}8 - 11{\cdot}4p)n_2' - 9{\cdot}4n_2'^2] - (1165{\cdot}9n_6'' - 2{\cdot}3n_6''^2) - (1755{\cdot}0n_2'' - 10{\cdot}3n_2''^2) + 6{\cdot}5n_2''n_6''.$$

A similar formula held for heavy formaldehyde (CD_2O):

$$\nu = (28378 - 67p) + [(1173{\cdot}5 + 4{\cdot}1p)n_2' - 8n_2'^2] - (937{\cdot}8n_6'' - 3{\cdot}1n_6''^2) - (1713{\cdot}1n_2'' - 9{\cdot}0n_2''^2) + 7{\cdot}0n_2''n_6''$$

The agreement between the calculated and the observed frequencies is sufficiently impressive to make it certain that Brand's analysis is largely correct. One notes that the analysis introduces only the frequencies ν_2 and ν_6. It may be taken as strong evidence that in the upper state the C–O length has changed relatively to the ground state and that also the upper state is non-planar. ν_6'' changes by as many as 8 quanta for CH_2O and 11 quanta for CD_2O. The greater number for CD_2O is understandable since the amplitude of ν_6 (mainly involving movement of the H or D atoms) will be less for CD_2O than for CH_2O, the departure from planarity in the equilibrium upper states of the two molecules being the same. Table 1 shows how in various progressions for CD_2O the intensity

TABLE 1. *Intensities and assignments of bands in fluorescence spectrum of* CD_2O, *according to Brand.*

n_2''	n_6''	Intensity	n_2''	n_6''	Intensity	n_2''	n_6''	Intensity	n_2''	n_6''	Intensity
0	1	5	0	2	6	1	1	5	1	2	6
0	3	7	0	4	9	1	3	9	1	4	9
0	5	10	0	6	10	1	5	6	1	6	5
0	7	6	0	8	4	1	7	2			
0	9	1									
0	11	0									

increases up to *ca.* 5 quanta of ν_6''. This would be expected, by the Franck–Condon principle, for a non-planar upper state.

* Many authors call this b_2 (see footnote in Part I). In the present paper the definitions of b_1 and b_2 given in Part I have been adhered to.

Brand's analysis is not, however, complete. His formulæ contain the factor Xp in which p has to be given the value 1 if n_6'' is odd and 0 if n_6'' is even. Since ν_6 is not a totally symmetrical frequency, the total symmetry of the lower level differs according to whether n_6'' is even or odd. It therefore appeared that there were two principal fluorescing levels, one of which was able to combine with the ground state only when n_6'' was even and the other only when n_6'' was odd. The relation of these levels to each other was left unexplained.

Before we suggest more detailed interpretations of the fluorescence spectrum, however, let us first survey what is known of the absorption spectrum.

Absorption Spectrum of Formaldehyde.—The near ultra-violet absorption of formaldehyde stretches from *ca.* 3700 to *ca.* 2310 Å (Henri and Schou, *J. Chim. phys.*, 1928, **25**, 665; 1929, **26**, 1; Everett and Minkoff, *Trans. Faraday Soc.*, 1948, **44**, 816). The maximum intensity occurs at *ca.* 3400 Å. Henri and Schou classified the bands into series $A, B, C, D\cdots$; $B', C', D', E'\cdots$; $C''', D''', E'''\cdots$*; $C'', D'', E''\cdots$. The main bands $A, B, C, D\cdots$ in the longer-wave-length region (A lies at 3533 Å) form a progression with a separation of *ca.* 1180 cm.$^{-1}$. In dideuteroformaldehyde the separation is almost identical (Ebers, quoted by Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 112). This implies that the vibration is almost completely localized in the CO group, in accordance with its representing the totally symmetrical ν_2 C=O valency vibration which has a frequency 1744 cm.$^{-1}$ in the ground state of CH_2O and 1700 cm.$^{-1}$ in the ground state of CD_2O. The drop in frequency implies a big lengthening of the C=O bond in the upper state, which fits with the fact that the progression does not reach maximum intensity until the sixth member and that the whole transition occupies an extensive range of the spectrum. $A, B, C\cdots$ thus form a ν_2' progression. $B', C', D'\cdots$, $C''', D''', E'''\cdots$, and $C'', D''\cdots$ probably represent further ν_2' progressions. The $B', C', D'\cdots$ separations, however, are a little greater than those of the $A, B, C\cdots$ series; or, put in another way, the separations A–B', B–C', C–$D'\cdots$ increase towards shorter wave-lengths. The interpretations of the first members of these progressions (*viz.*, A, B', C''', C'') remain to be determined.

Towards shorter wave-lengths, the regularity and nature of the spectrum change. It is discrete to *ca.* 2750 Å, but diffuse thenceforward. The disturbance may be exemplified by the behaviour of the $A, B, C\cdots$ progression. At band G the fine structure begins to become more complex and more diffuse, the bands becoming completely diffuse after band H (*ca.* 2750 Å). Even at band F some perturbation of the progression occurs, as is evident from the separations given in Table 2. The separation E–F is greater than expected. Similar statements apply to bands G''' and G' in the spectrum. A continuous

TABLE 2. *Separations (cm.$^{-1}$) of the main bands in the absorption spectrum of formaldehyde. Measurements from Schou* (J. Chim. phys., 1929, **26**, 24).

A		*B*		*C*		*D*		*E*		*F*
28,278		29,464		30,630		31,771		32,900		34,032
	1186		1166		1141		1129		1132	

background is present from *ca.* 2670 Å onwards. Hydrogen atoms are produced by absorption of wave-lengths at least as great as 3130 Å (Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176). It appears obvious that at least one further electronic transition is concerned in the spectrum towards shorter wave-lengths.

To the long-wave-length side of A occurs a weaker band (called α), at 3703 Å. Earlier authors have pointed out that this almost certainly represents a $0\leftarrow\!\!-1$ band of the electronic transition, involving one of the possible ground state frequencies. The observed temperature dependence of the intensity of α (Reid and Dyne, personal communications, which revise a statement to the contrary by Schüler and Reinebeck, *Z. Naturforsch.*, 1950, **5***a*, 604) supports this identification, as does the fact that the band is comparatively strong in the fluorescence spectrum.

* Henri and Schou found an earlier band B''' of this progression. Dr. Brand has informed the author, however, that his own plates do not support the existence of such a band; though they show a progression in addition to those listed by Henri and Schou, starting at 28,744 cm.$^{-1}$ (3479 Å).

The only principal band common to the fluorescence and absorption spectra is the α one, though in addition (Brand, personal communication) (i) a band at 26,569 cm.$^{-1}$ appears weakly in both spectra and (ii) bands called β and γ (see Table 3 below) appear in the fluorescence spectrum excited by a discharge at low pressures and also in the absorption spectrum of CD_2O (they probably appear also in the absorption spectrum of CH_2O, but are overlain by bands A and B).

Dieke and Kistiakowsky (*Phys. Review*, 1934, **45**, 4), from a study of the rotational fine structures, showed that the bands A, B, C, B', C', and C''' were perpendicular, being polarized in the plane of the molecule and parallel to the H···H line (CH_2O is an approximately symmetric top molecule with the axis of least moment of inertia along the C=O line). Presumably therefore each band in the A, $B\cdots$, B', $C'\cdots$, and C''', $D'''\cdots$ progressions is polarized in this way. No definite evidence exists for the C'', $D''\cdots$ bands, but Dieke and Kistiakowsky state that certain bands in the spectrum appear to be of the parallel type, a statement that probably refers to the C'', $D''\cdots$ bands. The extra progression observed by Brand and beginning at 28,744 cm.$^{-1}$ also appears to consist of parallel-type bands (Brand, personal communication). The bands analysed by Dieke and Kistiakowsky show an intensity alternation of the sub-bands; this implies that the upper states of the A, $B\cdots$, B', C', $\cdots$ and C''', $D'''\cdots$ progressions are planar or nearly so. The rotational constants found by Dieke and Kistiakowsky do not differ much from band to band. It is consistent with their analysis therefore (though not absolutely certain) that the analysed bands have the same electronic lower level (probably the vibrationless ground state) and also the same electronic upper state (though with different superimposed vibrations).

The rotational fine structure of the α band in absorption has also been partly analysed (Dyne, *J. Chem. Phys.*, 1952, **20**, 811). The structure of the part analysed is qualitatively the same as that found by Dieke and Kistiakowsky for the bands of shorter wave-length. The sub-bands again show an intensity alternation, implying that the upper state is not far from planar. The rotational constants are consistent with the band's having the same lower electronic state and also the same upper electronic state as the bands studied by Dieke and Kistiakowsky. The temperature dependence, however, shows that the lower level of α is not vibrationless. Determination of the K'' numbering shows that the lower level has total symmetry B_1 or B_2; which makes it practically certain that the lower level is the ground state with one quantum of the $\nu_5 b_2$ or one quantum of the $\nu_6 b_1$ vibration. The spacing of the sub-bands in α and in the fluorescence progression to which it belongs is not quite the same as in the absorption bands studied by Dieke and Kistiakowsky. Brand (*Trans. Faraday Soc.*, 1950, **46**, 805), assuming the rotational constants of the A band to apply to the fluorescence bands, has shown that this can be accounted for by a Coriolis interaction between the ν_5 and ν_6 fundamentals. According to Dyne, the α band appears to be double, the short-wave-length part having the lower level $n_6'' = 1$ and the long-wave-length part $n_5'' = 1$.

Interpretations of the Spectrum.—At the outset we have to decide whether the bands A, $B\cdots$ belong to (1) a different, or (2) the same, electronic transition as all the fluorescence bands including α. The rotational analyses are certainly consistent with (2), but it is difficult to be certain. The main fact in support of (1) is the failure of A, $B\cdots$ to appear in fluorescence. Because of this, Schüler and Reinebeck (*loc. cit.*) have adopted hypothesis (1). They suppose the fluorescence system to involve a triplet upper state and the long-wave-length part of the absorption system (bands A, $B\cdots$) a singlet upper state. Their particular analysis supposes α to arise from the vibrationless level of the ground state, which now appears to be definitely wrong in view of the revised data on the temperature dependence of α in absorption. Moreover, if the A, $B\cdots$ bands involve an upper state different from that of the fluorescence bands, it is remarkable that both upper states should have practically the same value of ν_2' (cf. Table 2 and Brand's formula for the fluorescence bands), and that A, $B\cdots$ should in fact occur in just the positions predicted by Brand's formula. Further, assuming α to arise from the $n_5'' = 1$ or $n_6'' = 1$ level of the ground state and allowing for the resulting Boltzmann factor, we find that the intensity of α in absorption is much too great, relatively to that of A, for α to belong to a triplet←singlet

transition and A to a singlet←singlet transition (Dyne, *loc. cit.*). It appears that the balance of the evidence favours the same upper state for A, $B\cdots$ and the fluorescence bands, though one cannot rule out hypothesis (1) with certainty.

If we accept the supposition that A and α belong to the same electronic transition, we have then to interpret the observed separation of A and α, and to try to explain why A does not appear in fluorescence. The separation of A and α is *ca.* 1277 cm.$^{-1}$. Two interpretations of this separation may be given.

(i) Brand's analysis of the fluorescence bands suggests there are two fluorescing levels separated by 113 cm.$^{-1}$. The upper of these levels only combines with the ground state when n_6'' is even, the lower only when it is odd. An obvious possibility is to interpret the figure 113 cm.$^{-1}$ as the frequency $\nu_6'b_1$ in the upper state. If then the upper state were $^{e1}A_2$, its total symmetry would be $^1A_2$ or $^1B_2$ according as n_6' was 0 or 1. A $^1A_2$ level would combine with a $^1B_1$ lower level (n_6'' odd) but would not combine with a $^1A_1$ lower level (n_6'' even), whereas a $^1B_2$ level would combine with a $^1A_1$ lower level but not with a $^1B_1$. This interpretation has been adopted by Dyne (*loc. cit.*). It implies that α is a transition from the level $n_6'' = 1$ to the vibrationless level of the upper state and A is a transition from the vibrationless ground state to the level $n_6' = 1$ of the upper state. The interpretation of the 1277 cm.$^{-1}$ between A and α is therefore 1166 + 113 cm.$^{-1}$. α is a (0,1) band, A is a (1,0) band, and the two form part of a symmetry-forbidden electronic transition. The interpretation of the upper state as $^{e1}A_2$ is certainly in accord with expectations from our Figure. However, if we assume, with all previous workers, that the upper state is planar, the interpretation of 113 cm.$^{-1}$ as ν_6' is quite unconvincing. There is no precedent in the known spectra of molecules for production by a low-lying single-electron jump of such an enormous reduction of a vibrational frequency as 1166 to 113 cm.$^{-1}$. Because of this difficulty in interpreting the A–α separation as the sum of a ground-state and an upper-state frequency, the lowest ground-state frequency reported being 1166 cm.$^{-1}$, earlier authors (see Sponer and Teller, *loc. cit.*; Herzberg, " Infra-red and Raman Spectra," van Nostrand, New York, 1945) were led to question the correctness of the ground-state frequencies. Brand's analysis of the fluorescence spectrum, however, leaves no doubt of the correctness of the 1166 cm.$^{-1}$ ground-state frequency.

Another objection to interpreting the upper state as planar and $\nu_6' = 113$ cm.$^{-1}$ is that we should then expect fluorescence to occur from levels with $n_6' > 1$ and we might expect absorption bands to a level with $n_6' = 3$ (*i.e.*, *ca.* 226 cm.$^{-1}$ from A) to appear; neither of these expectations is realized. (A further, minor objection to interpretation of 113 cm.$^{-1}$ as ν_6' is that in writing a formula to express the observed frequencies as accurately as possible one then has to include a cross term between n_2' and n_6' which is of opposite sign to Brand's cross term between n_2'' and n_6''. However, the measurements of the fluorescence bands given by Brand are from low-dispersion spectrograms; and, as Dyne has pointed out, the band origins may differ appreciably from Brand's measurements, so that the data for a thoroughly satisfactory analysis do not exist and the present objection to $\nu_6' = 113$ cm.$^{-1}$ may not be significant.)

If, as the present series of papers and Brand's vibrational analysis strongly suggest, the upper state is non-planar, then a possible loophole exists in our main objection to $\nu_6' = 113$ cm.$^{-1}$. At first sight, if the upper state is non-planar, it is even more difficult to accept $\nu_6' = 113$ cm.$^{-1}$; for we should expect the bending to oppose any considerable decrease of ν_6 or even to increase it [cf. the bending frequency in the first excited state of acetylene (Part III)]. However, both the present theory and the rotational analysis suggest that the departure from planarity is not great. One has therefore to take into account the possibility of inversion in the upper state.* The appropriate symbols for the vibrations and orbitals of a C_{2v} molecule may be defined as follows:

	σ_v	σ_h		σ_v	σ_h		σ_v	σ_h		σ_v	σ_h
a_1	+	+	b_1	+	−	a_2	−	−	b_2	−	+

where σ_h stands for a reflection in the plane of the molecule. These definitions come to the same thing as those based on $C_2(z)$ and σ_v given and explained in Part I. If the CH_2O

* I am indebted to one of the referees for stressing this to me, though not in the present context.

molecule becomes far from planar, the appropriate symbols become a' and a'' according to whether a + or a − is placed in the σ_v column—the σ_h column is no longer appropriate. If the molecule is far from planar the bending-vibrational levels may simply all be described as a'. If, however, the departure from planarity is only slight, these levels occur in pairs. The spacing is then alternately short and long. The lower level of each pair is symmetrical with respect to reflection in the (lost) molecular plane of symmetry and may still be described as a_1. The upper level of each pair is anti-symmetrical with respect to reflection in the (lost) plane of symmetry and may still be described as b_1. If the molecule is far from planar, *i.e.*, has a high barrier to inversion, the levels in each pair become degenerate. If, however, the molecule is only slightly non-planar, *i.e.*, has a low barrier to inversion, the splitting of the levels may become appreciable. A diagram and discussion given by Herzberg (*op. cit.*, p. 222) make the situation clear. The splitting also decreases as the reduced mass of the molecule increases, *i.e.*, it should be less for CD_2O than for CH_2O. Further, the splitting should be most marked for the levels of the vibration which most affects the departure from planarity, *i.e.*, of the $\nu_6 b_1$ vibration in this case.

It might be possible therefore for 113 cm.$^{-1}$ to represent the splitting of the first vibrational level of the expected slightly non-planar upper state of CH_2O. The corresponding figure for CD_2O is less (67 cm.$^{-1}$), as expected. The lowest vibrational level would be appropriately described as having symmetry a_1, the next (113 cm.$^{-1}$ higher) b_1, the next (higher by an amount considerably greater than 113 cm.$^{-1}$) a_1, and so on. Only by assuming a non-planar upper state and taking account of the possibility of inversion does it seem reasonable to interpret 113 cm.$^{-1}$ as a vibrational spacing. (The known inversion splitting of the lowest levels of NH_3 is much less than 113 cm.$^{-1}$., *viz.*, 0·8 cm.$^{-1}$ for the vibrationless level, 36 cm.$^{-1}$ for $n_2 = 1$, but the departure from planarity may be much less in the excited state of CH_2O than in the ground state of NH_3 and so may more than offset the greater reduced mass of CH_2O. It is known that the splitting increases very rapidly as the vibrational quantum number increases or as the height of the potential barrier to inversion decreases.)

Neither Dyne nor Brand analysed the absorption spectrum beyond band *A*. We know from the rotational analyses that, if bands B' and C''' are assumed to arise from the vibrationless ground state, they behave like $^1B_2 \longleftarrow {}^1A_1$ transitions. B' and C''' are 825 and 1353 cm.$^{-1}$, respectively, from *A*. Just as *A* is interpreted as the transition to the $n_6' = 1$ level, either B' or C''' might be interpreted as the transition to the $n_6' = 3$ level of the upper state. " Normally " the *A*–B' and probably the *A*–C''' separations would be regarded as too small for this to be likely, but, because of the possible alternate short and long spacing of the ν_6' vibrational levels, the interpretation is not unreasonable. The $n_6' = 3$ level would have the same total symmetry as the upper level of *A*, *viz.*, $^1A_2 \times b_1 = {}^1B_2$, and the polarization of the transition would be as observed. If *A* belongs to the same electronic transition as the fluorescence bands, one certainly expects *A* to have associated with it changes in n_6'. Moreover, the band apparently analogous to *A* in the spectrum of acetaldehyde (Part VII) has associated with it a progression in a frequency other than that of the C=O stretching vibration, so that one expects *A* to have associated with it bands other than *A*, *B*, *C* ···. The difficulty is that if only ν_2 and ν_6 are supposed to be involved in the fluorescence, one would expect only ν_2 and ν_6 to be involved in the corresponding absorption. While one of the bands B' and C''' might be interpreted as a transition to the $n_6' = 3$ level, the interpretation of the other is difficult to see. The need to interpret also C'' and the band at 28,744 cm.$^{-1}$ adds to the difficulty. Parallel bands can arise in a $^{e1}A_2 \longleftarrow {}^1A_1$ transition, but only if we invoke a b_2 in addition to a b_1 frequency. It looks as though the absorption spectrum involves *two* electronic transitions, and/or more frequencies than ν_6 and ν_2 must be invoked.

A possible explanation of the failure of band *A* to appear in fluorescence might be given as follows. According to Sponer and Teller (*loc. cit.*) the temperature dependence of the intensity of α and the intensity of α in relation to *A* suggest a Boltzmann factor corresponding to only 600 or 700 cm.$^{-1}$. According to the present analysis, the Boltzmann factor should correspond to 1166 cm.$^{-1}$. It appears therefore that α may be appreciably

stronger than is expected on the basis of a Boltzmann factor alone. The explanation is presumably that the intensity is increased because of the Franck–Condon principle, in accord with the expected non-planarity in the upper state. In emission, A will be weak relatively to α, partly because of a Boltzmann factor corresponding to 113 cm.$^{-1}$ and partly because of the effect of the Franck–Condon principle.

A main difficulty with this interpretation (as indeed with any other) of the fluorescence and absorption spectra is to achieve certainty. The explanations, as far as they go, appear possible but unproved. We turn now to the second interpretation of the A–α interval.

(ii) It may be significant that the separation of $\nu_5''b_2$ and $\nu_6''b_1$ (1280—1166 cm.$^{-1}$) is just about 113 cm.$^{-1}$. Further, the corresponding separation for CD_2O (990—938 cm.$^{-1}$), within the accuracy with which the data are known, is equal to 67 cm.$^{-1}$ which corresponds to 113 cm.$^{-1}$ for CH_2O. In other words, the separation of A and α is just equal to the ν_5'' frequency for both CH_2O and CD_2O. The separations are 28,313 − 27,036 = 1277 cm.$^{-1}$ and 28,380 − 27,376 = 1004 cm.$^{-1}$, respectively. It seem unlikely that these agreements are coincidental.

The supposition that ν_5 is involved receives support from Noyes' statement (*Trans. Faraday Soc.*, 1937, **33**, 1495) that the $\nu_5''b_2$ frequency is involved in the near-ultra-violet absorption spectrum of acetone. We may also note that in-plane deformation is known to occur in the 2600-Å absorption of benzene and may have fundamentally the same cause as is involved with formaldehyde. It is possible to suggest an explanation of the occurrence of ν_5 in the spectrum. If X is the mid-point of the H · · · H line, ν_5 is a vibration that causes bending of the XCO line in the plane of the molecule. From the arguments given in Parts I and II we should expect this bending to tend to occur when an orbital is occupied that is largely built from a p orbital on the C atom which has its axis in the molecular plane. There are two b_2 orbitals occupied in the ground state of CH_2O. One is largely in the CH_2 group and the other largely on the O atom. The former is probably built more from the appropriate H_2 group orbital than from the C p orbital. When an electron is excited from the O b_2 orbital [as in (4)], however, the coefficients of the components of the CH_2 b_2 orbital will change, *i.e.*, there will be a change in the restoring forces controlling in-plane bending. Hence we may expect the ν_5b_2 vibration to be aroused. If so, in the excited state the XCO line may be regarded as slightly bent in the molecular plane, much as in a certain excited state of CH_3I the I atom lies slightly off the 3-fold axis of the CH_3 group (see Part VIII). One expects the bending to be very slight, however, so that ν_5 is unlikely to be involved to an extent of more than one quantum.

Suppose we accept the fact that ν_5'' is involved in the fluorescence spectrum along with ν_2'' and ν_6''. A is then a vibrationless electronic transition. The small *short*-wave-length shift that this band undergoes in CD_2O is in accord with the usual behaviour of a vibrationless band on substitution of deuterium for hydrogen. α is the $n_5'' = 1$ band. It becomes possible to alter Brand's formula for CH_2O to the following which now contains no mysterious factor 113·2 cm.$^{-1}$:

$$\nu = 28312{\cdot}7 + (1190n_2' - 12n_2'^2) - (1165{\cdot}9n_6'' - 2{\cdot}3n_6''^2) - (1755{\cdot}0n_2'' - 10{\cdot}3n_2''^2) + 6{\cdot}5n_2''n_6'' - (1280n_5'' - 3n_5''^2) + 4n_5''n_6'' + 7n_2''n_5''$$

The corresponding formula for CD_2O is

$$\nu = 28378 + (1183n_2' - 8n_2'^2) - (937{\cdot}8n_6'' - 3{\cdot}1n_6''^2) - (1713{\cdot}1n_2'' - 9{\cdot}0n_2''^2) + 7{\cdot}0n_2''n_6'' - (1000n_5'') + 5{\cdot}5n_5''n_6'' + 5n_2''n_5''$$

Table 3 shows the new assignments for the bands and the observed and calculated values of the frequencies. The agreement is about as good as that given by Brand with the old assignments.

It will be observed that only lower-state levels of total symmetry $^1A_1$ or $^1B_2$ occur. Bands to lower $^1A_2$ (*e.g.*, $^{e1}A_1 \times b_1 \times b_2$) or $^1B_1$ (*e.g.*, $^{e1}A_1 \times b_1$) levels do not occur. n_5'' is never more than one. n_6'' is always even. The lower levels of the A and α bands are respectively $^1A_1$ and $^1B_2$. According to the analysis, these bands have a common upper level. Yet it is known that both bands are perpendicular. This is impossible if the upper level is singlet. One is thus driven to the conclusion that the upper level is triplet.

It is necessary to enquire what the total symmetry of the upper level will be when the effect of the triplet spin operator on the space wave function is taken into account. The product representations of spin and orbital function for C_{2v} symmetry have been given by McClure (*J. Chem. Phys.*, **1949**, **17**, 665) and by Weissman (*ibid.*, **1950**, **18**, 232, 1258). It is readily seen from these that the transition $^3A_2 \longrightarrow {}^1A_1$ may proceed by mixing with (*i.e.*, "stealing" intensity from) any of the three allowed transitions $^1A_1 \longrightarrow {}^1A_1$ (*z*-polarized), $^1B_1 \longrightarrow {}^1A_1$ (*x*-polarized), or $^1B_2 \longrightarrow {}^1A_1$ (*y*-polarized),* provided that the

TABLE 3. *New assignments and calculated frequencies. Observed frequencies of band centres according to Brand.*

	n_2'	n_2''	n_5''	n_6''	Total ground-state symmetry	CH_2O $\nu_{obs.}$ cm.$^{-1}$	CH_2O $\nu_{calc.}$ cm.$^{-1}$	CD_2O $\nu_{obs.}$ cm.$^{-1}$	CD_2O $\nu_{calc.}$ cm.$^{-1}$
Band "*B*"	1	0	0	0	$^1A_1$	29,495	29,491	29,553	29,553 (Observed in absorption only)
Band γ ...	2	0	1	0	$^1B_2$	29,359	29,369(5)	29,715	29,714
Band "*A*"	0	0	0	0	$^1A_1$	28,313	28,313	28,380	28,378 (Observed in absorption only)
Band β ...	1	0	1	0	$^1B_2$	28,207	28,214	28,550	28,553
	1	0	0	2	$^1A_1$	27,173 *	27,168	27,690	27,690
Band "α"	0	0	1	0	$^1B_2$	27,036	27,036	27,376	27,378
	0	1	0	0	$^1A_1$	26,569 *	26,568	—	—
	1	1	1	0	$^1B_2$	26,470	26,476	—	—
	1	0	1	2	$^1B_2$	—	—	26,704	26,701
	0	0	0	2	$^1A_1$	25,990	25,990	26,515	26,515
	1	0	0	4	$^1A_1$	—	—	25,848	25,851
	0	1	1	0	$^1B_2$	25,297	25,298	25,679	25,679
	0	0	1	2	$^1B_2$	24,721	24,721	25,524	25,526
	0	1	0	2	$^1A_1$	24,258	24,258	24,824	24,825
	0	0	0	4	$^1A_1$	23,687 *	23,686	24,675	24,676
	0	2	1	0	$^1B_2$	23,579	23,581	24,003 *	23,998
	0	1	1	2	$^1B_2$	22,997	22,996	23,840	23,840
	0	0	1	4	$^1B_2$	—	—	23,698	23,698
	0	2	0	2	$^1A_1$	22,547	22,547	23,154	23,153
	0	1	0	4	$^1A_1$	21,970 *	21,967	22,999	23,000
	0	3	1	0	$^1B_2$	21,881 *	21,883	22,344 *	22,335
	0	0	0	6	$^1A_1$	21,393	21,400	22,863	22,863
	0	2	1	2	$^1B_2$	21,294	21,292	22,174 *	22,174
	0	1	1	4	$^1B_2$	—	—	22,029	22,027
	0	0	1	6	$^1B_2$	—	—	21,899	21,896
	0	3	0	2	$^1A_1$	—	—	21,499	21,499
	0	2	0	4	$^1A_1$	—	—	21,340	21,342
	0	4	1	0	$^1B_2$	20,207 *	20,211(5)	—	—
	0	1	0	6	$^1A_1$	—	—	21,201	21,201
	0	0	0	8	$^1A_1$	19,125 *	19,133	21,075	21,074
	0	3	1	2	$^1B_2$	19,613	19,607	20,528	20,525
	0	2	1	4	$^1B_2$	—	—	20,375	20,374
	0	1	1	6	$^1B_2$	—	—	20,243	20,239
	0	0	1	8	$^1B_2$	—	—	20,122	20,118
	0	2	0	6	$^1A_1$	—	—	19,552	19,557
	0	3	1	4	$^1B_2$	—	—	18,750	18,739
	0	2	1	6	$^1B_2$	—	—	18,609	18,600
	0	1	1	8	$^1B_2$	—	—	18,479	18,475
	0	0	1	10	$^1B_2$	—	—	18,366	18,365
	0	1	0	10	$^1A_1$	—	—	17,672	17,676

* These bands are overlapped each by another transition.

energies of these are sufficiently similar. In the same way, the transition $^3A_2 \longrightarrow {}^1B_2$ may proceed by mixing with either of the two allowed transitions $^1A_1 \longrightarrow {}^1B_2$ (*y*-polarized) or $^1B_2 \longrightarrow {}^1B_2$ (*z*-polarized). On the other hand, the transition $^3A_2 \longrightarrow {}^1A_2$ can only occur by mixing with either of the two allowed transitions $^1B_1 \longrightarrow {}^1A_2$ (*y*-polarized) or $^1B_2 \longrightarrow {}^1A_2$ (*x*-polarized), while the transition $^3A_2 \longrightarrow {}^1B_1$ can only occur by mixing with one of the two allowed transitions $^1A_1 \longrightarrow {}^1B_1$ (*x*-polarized) or $^1B_1 \longrightarrow {}^1B_1$ (*z*-polarized).

* As used here, the *z*-axis is in the plane of the molecule and bisects the HCH angle; the *y* axis is in the molecular plane and parallel to the H···H line; the *x* axis is perpendicular to the molecular plane. McClure and Weissman interchange the *x* and the *y* axis.

Presumably the intensity of a forbidden transition in the near-ultra-violet region is "stolen" from the first really strong transition of the formaldehyde molecule which occurs at *ca.* 1745 Å. The absorption at 1745 Å is to be interpreted either as the first member of a "*s*" Rydberg series, *viz.*,

$$\cdots(b_2)(3sa_1),\ {}^1B_2 \longleftarrow \cdots(b_2)^2,\ {}^1A_1$$

where $3sa_1$ stands for a 3*s* orbital on the O atom (Walsh, unpublished work); or as

$$\cdots(b_2)(\bar{a}_1),\ {}^1B_2 \longleftarrow \cdots(b_2)^2,\ {}^1A_1$$

where $\bar{a}_1$ is the highest orbital shown in our Figure (McMurry and Mulliken, *loc. cit.*). In either case, the absorption represents a ${}^1B_2 \longleftarrow {}^1A_1$ transition. The upper state of the fluorescence bands lies almost midway between the ground state and the upper state of the 1745-Å system. One may suggest therefore that only those triplet$\longleftrightarrow$singlet transitions will occur in the near-ultra-violet region that are able to mix with the strong ${}^1B_2 \longleftrightarrow {}^1A_1$ transition. This implies that all the triplet$\longleftrightarrow$singlet bands must be *y*-polarized. Presumably the triplet upper state may be perturbed by either end of the ${}^1B_2 \longleftrightarrow {}^1A_1$ transition, provided the resulting bands are *y*-polarized. It follows that, if the upper state of the fluorescence bands is ${}^3A_2$, transitions will only be observed to ground-state levels that have total symmetry ${}^1A_1$ or ${}^1B_2$. Further, it is readily seen that no other triplet upper state can be substituted for ${}^3A_2$ in order to explain the observed facts. It is satisfactory that the conclusion that the upper state must be ${}^3A_2$ accords with the expectation from our Figure that ${}^3A_2$ is the only triplet state likely to be involved.

To recapitulate, (1) acceptance of the vibrational analysis given above forces the conclusion that the upper state is triplet and that the upper state is in fact ${}^3A_2$; (2) the ${}^3A_2$ upper level gives rise to fluorescence bands that proceed only to ${}^1A_1$ or ${}^1B_2$ lower levels and are always *y*-polarized; (3) the ${}^3A_2$ upper level behaves as ${}^1B_2$ when it combines with ${}^1A_1$ lower levels, and as ${}^1A_1$ when it combines with ${}^1B_2$ lower levels, in agreement with the vibrational analysis and the polarization data.

Interpretation of the long-wave-length end of the absorption spectrum as a triplet$\leftarrow$singlet transition is not ruled out on intensity grounds. The extinction coefficients for triplet$\leftarrow$singlet transitions in light molecules are less than unity (Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 72). Unfortunately, the extinction coefficients for the formaldehyde near-ultra-violet absorption are not known. In aqueous solution formaldehyde is hydrated and polymerized. In hexane at $-70°$ the rate of polymerization is sufficiently slow for the spectrum of the monomer to be obtained (Schou, *J. Chim. phys.*, 1929, **26**, 72), but sufficiently fast to preclude measurement of the extinction coefficients because of the difficulty of knowing the concentration of monomer. A further difficulty is that the whole near-ultra-violet absorption, as we have seen, undoubtedly involves more than one electronic transition. It should be stressed that the tentative conclusion that the upper state is triplet applies only to the fluorescence bands and to certain of the longest-wave-length bands of the absorption spectrum. It probably applies in fact only to that part of the absorption spectrum which corresponds to the long-wave-length tail of the absorption spectrum of acetaldehyde (see Part VII). For acetaldehyde the extinction coefficients are known; the long-wave-length tail stretches from *ca.* 3300 to 3400 Å and has $\varepsilon_{max.} \sim 0{\cdot}1$—$0{\cdot}2$. It is probable therefore that the extinction coefficient of the corresponding part of the formaldehyde absorption agrees with Kasha's rule.

It is of particular interest, as Burawoy has pointed out, that the origin of the first electronic absorption system in formaldehyde is moved towards shorter wave-lengths as a result of methyl substitution (see Part VII). This is the opposite of the usual effect of methyl substitution and may have an important bearing on the nature of the transition involved.

The failure of band *A* to appear in fluorescence might be explained essentially as suggested above in our discussion of the first alternative interpretation of the *A*–α interval. According to Dyne, α in absorption is about 1/20 as intense as *A*. According to Sponer and Teller, it is about 1/15 as intense. If α represents the $n_5'' = 1$ band, then in absorption at room temperature the Boltzmann factor leads to the expectation that the intensity ratio of $\alpha : A$ should be *ca.* 1/450. α is thus much stronger than it is expected to

be on the basis of the Boltzmann factor alone. Presumably an intensity factor due to the Franck–Condon principle is important. It follows that, in emission, A (having, according to the present interpretation, the same upper level as α) should be weaker than α by a factor of 23—30 and may therefore not be observed.

It is readily shown from the symmetries of the spin operator given above that, in absorption from the vibrationless ground state to an $^3A_2$ upper state, only those bands will appear for which the upper state has vibrational symmetry a_1, b_2 or a_2. A transition to $^3A_2$ with vibrational symmetry b_1 could not mix with the allowed $^1B_2 \leftarrow\!\!- {}^1A_1$ transition. This means that the absorption bands which arise from the vibrationless ground level and belong to the triplet←singlet transition have vibrational interpretations limited to an odd number of quanta of b_2-vibrations, a quantum of any totally symmetrical vibration, an even number of quanta of either a b_2- or the b_1-vibration, or an odd number of quanta of b_2-vibrations in combination with an odd number of quanta of the b_1-vibration. The analysis of the fluorescence spectrum makes it probable that the only b_2-vibration which need be considered is ν_5 and that only one quantum of this will be present. B' and C''' could be interpreted in terms of these expectations. (The fact that the separations in the B', $C' \cdots$ progression are rather larger than in the A, $B \cdots$ progression may well be due to a positive interaction term between a bending and a stretching frequency such as is known to occur in the ground state vibrational formula for CO_2. The increasing separation A–B', B–C' . . . of course follows from the greater spacings in the B', $C' \cdots$ than in the A, $B \cdots$ progression.)*

On the triplet←singlet explanation, however, it seems certain that, if the z-polarization of C'' and the band at 28,744 cm.$^{-1}$ is confirmed, these bands belong to a separate absorption transition, perhaps to the upper state (3).

It should be emphasized that the analysis depends on the assumption that the separation of A and α is not *accidentally* equal to ν_5''. As long as this is granted, it follows inevitably that the upper electronic state cannot be singlet. In essence, the argument is that one of the lower levels of the two bands must then belong to species A and the other to species B, and that both bands must have a common upper level. In that case, the fact that both bands are perpendicular means that the common upper level, whatever its species, cannot be singlet. On the other hand the conclusion that the upper state is triplet is not without serious difficulties. One of these is that one might have expected from the ready polymerization of formaldehyde that the lowest triplet state (expected to be $^3A_2$) would lie considerably lower than 80 kcal./mole above the ground state. Another difficulty lies in the fine structure of the α band. According to Brand and Dyne this fine structure implies that the short-wave-length portion of α has the lower level $n_6'' = 1$, not $n_5'' = 1$. Further, the long-wave-length component of α remains unexplained. On the present interpretation, the transition from $n_6'' = 1$ to the vibrationless upper state would lie to the *violet* side of the $n_5'' = 1$ band, but, having a $^1B_1$ lower level, would not be expected to occur. Finally, if the triplet←singlet interpretation is correct, the $^1A_2 \leftarrow\!\!- {}^1A_1$ transition (and possibly other transitions) remain to be identified in the shorter-wave-length portions of the near-ultra-violet absorption.

The final interpretation of the near-ultra-violet spectrum of formaldehyde must thus await further work. However, there is no doubt that the correlation diagram (p. 2307) and the deductions that can be made from it about the shapes expected for the low-lying excited states are likely to prove useful in achieving a final satisfactory interpretation.

The author is most grateful to Drs. Dyne and Brand for discussion and correspondence.

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* Herzberg (*Trans. Faraday Soc.*, 1931, **27**, 378) suggests that the A–B' separation represents the in-plane, totally symmetrical, CH bending frequency which is 1503 cm.$^{-1}$ in the ground state. The appearance of ν_3 would not be surprising since it is improbable that the angle HCH remains exactly equal to the angle HCO when the molecule is excited. More probably angle HCH changes relatively to angle HCO, and ν_3 may occur in consequence. However, ν_3 is not involved in the fluorescence spectrum and also the drop from 1503 to *ca.* 830 cm.$^{-1}$ seems rather large. Possibly 830 cm.$^{-1}$ represents ν_5'.

472. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VII.* A Note on the Near-ultra-violet Spectrum of Acetaldehyde.*

By A. D. Walsh.

The near-ultra-violet spectrum of acetaldehyde, like that of formaldehyde, consists of at least two electronic transitions. This makes analysis difficult, but the following definite points emerge. Ground-state fundamental frequencies of *ca.* 630 and 779 cm.$^{-1}$ suggested by Thompson and Harris are confirmed. A further probable ground-state fundamental frequency is *ca.* 475 cm.$^{-1}$. The long-wave-length end of the spectrum involves an excited state frequency of *ca.* 320 cm.$^{-1}$ which plausibly represents an out-of-plane bending of the $\begin{matrix}H\\C\end{matrix}\!>\!C\!=\!O$ group. The first electronic transition of formaldehyde is shifted to *short* wave-lengths by methyl substitution; but the second electronic transition probably to long wave-lengths.

In view of the analysis of the fluorescence and long-wave-length absorption bands of formaldehyde * it is of interest to consider the corresponding absorption system of acetaldehyde.

The near-ultra-violet absorption bands of acetaldehyde vapour have been measured by Schou (*J. Chim. phys.*, 1929, **26**, 27). Apart from his arrangement of the bands, which appears not to have any fundamental meaning, there seems to have been no previous attempt at analysis. The stronger bands begin with a band labelled *A* at *ca.* 3390 Å. The measurements and labels, according to Schou, of the eight longest-wave-length stronger bands are tabulated below. The measurements of bands *A*, *B*, and *a* represent origins taken from Schou's rotational analysis of these bands; those for bands *b* to *f* are approximate positions of the band centres. To the red side of band *A* occur four weak bands here labelled α, β, γ, δ. The Table shows the positions of the band centres. The separations of these from *A* are, respectively, 275, 475, 630, and 779 cm.$^{-1}$. There is no doubt that these bands represent transitions from vibrational levels of the ground state. The fundamental frequencies of the $CH_3{\cdot}CHO$ molecule have been discussed by Thompson and Harris (*Trans. Faraday Soc.*, 1942, **38**, 37) and Morris (*J. Chem. Phys.*, 1943, **11**, 230). The list of fundamentals suggested by the former authors includes a frequency (ν_3) of 780 cm.$^{-1}$ (in the Raman spectrum of the liquid; 764 cm.$^{-1}$ in the infra-red spectrum) and another (ν_2) of 650 cm.$^{-1}$ (in the Raman spectrum of the liquid; 625 cm.$^{-1}$ in the infra-red spectrum). The correspondence of these to the A–δ and A–γ separations makes it practically certain that *A* is a vibrationless band and δ, γ represent transitions from the $n_3'' = 1$ and $n_2'' = 1$ levels, respectively, of the ground state to the vibrationless upper state. It also makes it practically certain that 780 and 630 cm.$^{-1}$ represent fundamental frequencies of the ground state. This is in agreement with the suggestions of Thompson and Harris, but not with those of Morris who failed to observe the 625-cm.$^{-1}$ infra-red frequency.†

There seems no doubt ‡ that the 475-cm.$^{-1}$ separation of *A* and β also represents a ground-state fundamental frequency. Not only does the separation occur in the near-ultra-violet absorption of acetaldehyde, but also weak bands lying *ca.* 475 cm.$^{-1}$ to the red of the first strong bands of the 1818- and 1660-Å absorption systems are clearly visible on photographs of the far-ultra-violet spectrum of acetaldehyde taken by the author (Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 176). The actual measurements are

1818-Å System		1660-Å System	
54,515 cm.$^{-1}$	>481	59,689 cm.$^{-1}$	>481
54,996 ,,		60,170 ,,	

Since the separation is independent of the precise upper state being considered, it apparently represents a ground state frequency only. We shall call the vibration involved ν_x. β is

* Part VI, preceding paper.

† Pitzer and Weltner (*J. Amer. Chem. Soc.*, 1949, **71**, 2842), because of Morris's work, also discarded the 625-cm.$^{-1}$ frequency as a fundamental.

‡ Except that it might be possible to interpret β as a transition from the $n_2'' = 1$ level to the same upper level as that of *B*. The separation of β and *B* is 640 cm.$^{-1}$.

thus a transition from the $n_z'' = 1$ level of the ground state to the vibrationless upper state. Thompson and Harris's list does not include any frequency less than 520 cm.$^{-1}$. Morris records the " 520-cm.$^{-1}$ " fundamental at 509 cm.$^{-1}$ in the infra-red spectrum. He also gives another fundamental frequency at 421—431 cm.$^{-1}$, finding a strong band here in the infra-red spectrum, but Pitzer and Weltner (*loc. cit.*) cite evidence against *ca.* 426 cm.$^{-1}$ being a fundamental frequency. Probably the 475-cm.$^{-1}$ separation represents the *ca.* 520-cm.$^{-1}$ frequency of the infra-red spectrum. The agreement is not very good, but the measurements of the infra-red and the Raman spectrum do not agree very well. Thus Morris records the " 780-cm.$^{-1}$ " fundamental at 733—765 cm.$^{-1}$, the measurement in the Raman spectrum being 779—780 cm.$^{-1}$. ν_x, ν_2, and ν_3 undoubtedly represent deformation vibrations of some kind. The most probable interpretation is that they represent (not necessarily respectively) in-plane C–C–O bending, out-of-plane rocking of the H attached to the carbonyl group, and out-of-plane rocking of the CH_3 group (compare the discussion given by Morris, *loc. cit.*). These are all vibrations which, from our discussion of the corresponding formaldehyde transition, we might expect to occur in the spectrum. It is significant for the interpretation of the formaldehyde spectrum that bands should be associated with *A* of the acetaldehyde spectrum which form a progression in a frequency other than that of C=O stretching.

The interpretation of band α is less certain. There is no obvious band at *ca.* 275 cm.$^{-1}$ to the red side of the first strong bands of the shorter-wave-length transitions. It seems therefore that 275 cm.$^{-1}$ is not to be interpreted as a ground-state fundamental frequency, but as a difference between an upper-state frequency and a ground-state frequency. We shall return to this point below.

Frequencies and assignments of the long-wave-length absorption bands of acetaldehyde.

Intensity	Label	Band centre, cm.$^{-1}$	Assignment					$\nu_{calc.}$, cm.$^{-1}$
			n_y'	n_z'	n_x''	n_2''	n_3''	
1	δ	28,711	0	0	0	0	1	—
1	γ	28,860	0	0	0	1	0	—
1	β	29,015	0	0	1	0	0	—
1	α	29,215	—			—		—
3	*A*	29,490	0	0	0	0	0	—
2	*B*	29,655	0	1	0	0	0	—
4	*a*	29,800	1	0	0	0	0	29,808
3	*b*	29,974	1	1	0	0	0	29,973
6	*c*	30,136	2	0	0	0	0	30,122
4	*d*	30,272	2	1	0	0	0	30,287
6	*e*	30,358	3	0	0	0	0	30,432
5	*f*	30,499	3	1	0	0	0	30,597

The diagram of the spectrum given by Schou makes it very probable that bands *A*, *a*, *c*, and, probably, *e* form a progression in some upper-state frequency, while bands *B*, *b*, *d*, and *f* form another progression in the same upper-state frequency. We shall call this frequency ν_y. Except for the *e* and the *f* band the positions of the members of these progressions can be reproduced reasonably well (see Table) by adding the term $(320n_y' - 2n_y'^2)$ to the frequencies of the *A* and the *B* band. 320 cm.$^{-1}$ is thus an upper-state frequency. There is a steady increase in intensity in each progression. It therefore appears that the frequency is aroused by an appreciable change of shape of the molecule in the upper state. By analogy with formaldehyde the biggest change involving such a low frequency is likely to be an out-of-plane bending into a pyramidal form. It is plausible therefore to suggest that ν_y' represents an out-of-plane bending vibration of the $\begin{matrix} H \\ C \end{matrix}\!>\!C=O$ group. The separation of the *A* and the *B* band is 165 cm.$^{-1}$. This is shown in the Table as another upper-state frequency, ν_z', but its interpretation is quite uncertain.* It becomes possible that α represents a transition either from $n_2'' = 1$ to $n_y' = 1$ or from $n_x'' = 1$ to $n_z' = 1$. In either case however its separation from *A* is calculated to be 310 cm.$^{-1}$ (630 —

* It might represent the separation of two electronic states. In that case what is here called the " second " electronic transition would have to be re-labelled the " third " electronic transition.

320 = 475 − 165 = 310) which is not sufficiently close to the observed 275 cm.$^{-1}$ for the assignment, although possible, to be certain.

The observed frequencies of bands *e* and *f* do not agree at all well with the calculated frequencies, although from Schou's diagram they look as though they might well belong to the *A* and the *B* progression respectively. However, it is clear from at least two considerations that, starting around band *d*, the spectrum suffers considerable disturbance. First, the spacing and intensity succession of the bands thenceforward becomes quite different; secondly, the bands from *d* onwards begin to be diffuse whereas bands *A* to *C* have sharp fine structure. It seems very probable that a second electronic transition is concerned from somewhere around band *d* onwards. This is strongly supported by curves given by Schou (*J. Chim. phys.*, 1929, **26**, 77) for the absorption of acetaldehyde in solution in hexane or water. The absorption in hexane is shifted very little relatively to the vapour-phase absorption, although all vibrational structure is blotted out. In these solution curves, the absorption bands discussed here appear as a shoulder (log $\varepsilon_{max.}$ ~0·1—0·2) on the long-wave-length side of the main absorption (log $\varepsilon_{max.}$ ~1·1—1·2 at 2900 Å in hexane), being overtaken by the second (main) transition at *ca.* 3300 Å in the hexane solution, *i.e.*, just about where the vapour-phase band *d* lies. The occurrence of a second transition affecting the short-wave-length end of the first absorption system is also strongly to be expected from our knowledge of the formaldehyde absorption spectrum (cf. the discussion of the formaldehyde *A*, *B*, *C* . . . progression in Part VI). The acetaldehyde bands become completely diffuse at *ca.* 3190 Å (compare 2750 Å for formaldehyde), while eventually continuous absorption sets in. The absorption as a whole thus involves several electronic transitions. This is in accord with expectations from Part VI, but it makes analysis of the whole system difficult. It does not appear profitable at present to carry the vibrational analysis beyond band *f*.

Two further interesting points emerge, however. The positions of the bands β, γ, δ in relation to band *A* leave no doubt that *A* is the origin of the first electronic transition. *A* is at 29,490 cm.$^{-1}$. The frequency of the origin of the corresponding transition in formaldehyde was not greater than 28,313 cm.$^{-1}$. Methyl substitution thus causes this first transition to move to *short* wave-lengths.* On the other hand, the second transition becomes noticeable at *ca.* 30,287 cm.$^{-1}$ (band *d*) in acetaldehyde compared with *ca.* 34,032 cm.$^{-1}$ (band *F*) in formaldehyde. The position of the onset of complete diffuseness shows a shift in the same direction. Methyl substitution thus appears to cause the second electronic transition to move to long wave-lengths. It is for this reason that the wave-length range in which the first transition can be readily studied in acetaldehyde is so small, with the result that it is not possible to fix the unperturbed magnitude of the larger frequencies (*e.g.*, the C=O valency vibration) that would be expected to occur in the upper state.

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* The shift of the first transition, but not of the second, is in accord with general statements by Burawoy (*Discuss. Faraday Soc.*, 1950, **9**, 70).

473. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VIII.* Pentatomic Molecules:* CH_3I.

By A. D. Walsh.

The electronic orbitals of methyl iodide are discussed with particular reference to the three lowest-energy absorption transitions. It is shown that the first of these plausibly leads to dissociation of the molecule. In the equilibrium forms of the excited states of each of the other two transitions (i) the HCH angle should be markedly reduced and hence the totally symmetrical, CH_3-deformation vibration should appear strongly, (ii) the C–I bond should be lengthened a little and hence the C–I valence vibration should appear, probably less strongly, and (iii) the I atom should lie off the trigonal axis of symmetry of the CH_3 group and hence the ν_6e deformation vibration should appear and certain consequences be apparent in the fine structure of the bands. The observed spectrum confirms all these expectations.

In this paper the orbitals and shape of the methyl iodide molecule are discussed, with particular reference to the ultra-violet absorption regions corresponding to the three lowest energy levels. With minor changes, the ideas developed are applicable to the shapes and spectra of the other methyl halide molecules. The ground states of these molecules belong to the symmetry class C_{3v}. The definitions of the symbols appropriate to the orbitals of these molecules have been given in Part IV (*J.*, 1953, 2296).

Orbitals of Methyl Iodide.—The simplest way of obtaining the orbitals of the CH_3I molecule is to combine those of a CH_3 group (Part IV) with the valency orbitals of the I atom. Let us, in particular, superimpose a graph (*A*) of the binding energy of the orbitals of a CH_3 group plotted against HCH angle (Part IV) upon a graph of the binding energy of the valency orbitals of an isolated I atom also plotted against HCH angle. The latter graph will of course consist of horizontal straight lines. The I valency orbitals are the three I 5*p* atomic orbitals, which are degenerate in the isolated atom. When the atom is in the field of the CH_3 group this degeneracy is split. There are then two degenerate orbitals and a single orbital, which may be described, in symbols appropriate to C_{3v} symmetry, as $5pee$ and $5pa_1$, or in symbols appropriate to the local symmetry of the C–I bond in CH_3I as $5p\pi\pi$ and $5p\sigma$. In Fig. 1 the orbitals are represented with the three-fold degeneracy already split. For graph (*A*) we shall draw the a_1s_A–a_2'' and ee–$e'e'$ orbital curves as crossing (see footnote, p. 2303). For simplicity, in Parts IV and V no such crossing was shown; the reason for its introduction here will appear below. On the 120° ordinate the symbols appropriate to C_{3v} symmetry are of course retained for the CH_3 group orbitals, whereas those appropriate to D_{3h} symmetry were introduced in Parts IV and V.

Such a superposition is shown in Fig. 1. The CH_3 group orbitals are shown as broken lines (– – –) and the I atom orbitals as full lines. As the curves are drawn, the lines for the I $5pa_1$ and a_1s–a_1 orbitals cross. These orbitals have the same symmetry with respect to the operations appropriate to the CH_3I molecule. The crossing has therefore to be replaced by an " avoided crossing " shown dotted (. . . .) in the Figure. The meaning of the dotted curves that result is as follows. The lower dotted line corresponds to an in-phase interaction of the C atom hybrid valency (represented by the original a_1s_A–a_1 curve) with the I atom $5pa_1$ valency. In the ground state of the CH_3I molecule two electrons occupy this orbital which may be written symbolically as

$$[\mathrm{C(hybrid)} + \lambda \mathrm{I}(5p)]a_1\dagger$$

and gives rise to the main C–I bond. When the HCH angle is 109° this molecular orbital should be degenerate with the ee C–H bonding orbitals, the theory of tetrahedral molecules requiring a triply degenerate orbital. Strictly, this statement is true only for AB_4 molecules. For AB_3C molecules, where B and C are not of very different electronegativity, it is assumed to be approximately true, just as Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 209),

* Part VII, preceding paper.

† λ and μ are constants introduced to take account of the polarity of the orbitals, *i.e.*, of the unequal contributions of the C(hybrid) and I(5*p*) orbitals.

in drawing a correlation diagram for AB_2 molecules, assumed certain approximate orbital degeneracies when the apex angle was 60° which would only strictly occur for B_3 molecules. The I $5pa_1$ line is therefore drawn in Fig. 1 between the highest and the lowest point of the a_1s_A–a_1 curve. Unless it is so drawn there will be no bond formation beteeen the CH_3 lone-pair orbital and the I atom $5pa_1$-valency orbital, and no approximate triple degeneracy of the required three orbitals when the HCH=HCI angle is tetrahedral.

The upper dotted line in Fig. 1 corresponds to an out-of-phase interaction of the C atom hybrid valency with the I atom $5pa_1$ valency. The orbital may be symbolized as

$$[\text{C(hybrid)} - \mu\text{I}(5p)]a_1^*$$

and it is anti-bonding between the C and the I atom. In the ground state of the CH_3I molecule six of the orbitals shown in Fig. 1 are fully occupied. Some of the curves rise and some fall from left to right. One may therefore expect the HCH angle in the ground state to be intermediate between 90° and 120°. The observed value is 110° 58′ (Gordy, Simmons, and Smith, *Phys. Review*, 1948, **74**, 243). At this angle the anti-bonding C–I orbital is unoccupied in the ground state.

FIG. 1.

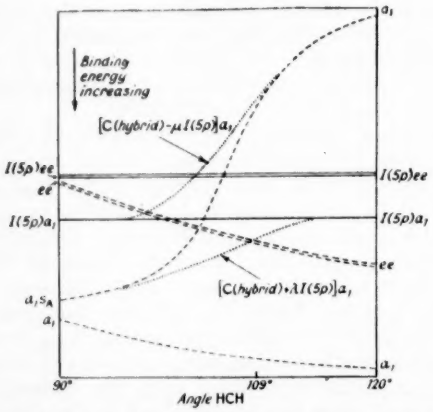
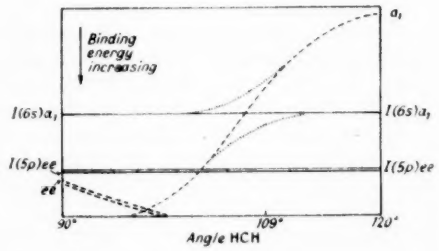


FIG. 2.



Spectrum of CH_3I: *Expectations.*—In order to discuss the longest-wave-length transitions of the CH_3I molecule we have to introduce a further I atom orbital, namely, the 6*s* orbital. The reason for this choice is the association of one of the transitions with a certain Rydberg series lying to shorter wave-lengths (see below). The symbol a_1 is applied to this orbital with respect to C_{3v} symmetry. It is shown as a full line in Fig. 2, which incorporates only the upper part of Fig. 1. One sees that as the curves are drawn the I $6sa_1$, and $[\text{C(hybrid)} - \mu\text{I}(5p)]a_1$ lines cross. These orbitals have the same symmetry with respect to the operations appropriate to the CH_3I molecule. The crossing has therefore to be replaced by an "avoided crossing," shown dotted in Fig. 2. The meaning of the dotted curves that result is as follows. The lower dotted line corresponds to an in-phase interaction of the $[\text{C(hybrid)} - \mu\text{I}(5p)]a_1$ orbital with the I $6sa_1$ orbital. Where the resulting curve is dotted, the orbital may be symbolized as

$$[[\text{C(hybrid)} - \mu\text{I}(5p)] + \zeta\text{I}(6s)]a_1\dagger \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

To the right of the dotted portion the orbital becomes simply the $\text{I}(6s)a_1$ orbital. Immediately to the left, it becomes the anti-bonding $[\text{C(hybrid)} - \mu\text{I}(5p)]a_1$ orbital. The upper dotted line corresponds to an out-of-phase interaction of the two orbitals. Where the resulting curve is dotted the orbital may be symbolized as

$$[[\text{C(hybrid)} - \mu\text{I}(5p)] - \eta\text{I}(6s)]a_1\dagger \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* λ and μ are constants introduced to take account of the polarity of the orbitals, *i.e.*, of the unequal contributions of the C (hybrid) and I(5*p*) orbitals.

† ζ and η are constants introduced to take account of the unequal contributions of the component orbitals.

To the left of the dotted portion the orbital becomes simply the I(6s)a_1 orbital. Immediately to the right it becomes the [C(hybrid) — μI(5p)]a_1. We are now in a position to discuss the lowest-energy transitions of the CH_3I molecule.

Clearly, from Fig. 2 and with an angle of *ca.* 109°, the lowest-energy transition should be of an electron from the I(5p)ee orbitals to the orbital symbolized as (1). This orbital has its minimum on the 90° ordinate. In the upper state the HCH angle therefore decreases. As it does so, the upper orbital becomes more purely the anti-bonding [C(hybrid) — μI(5p)]a_1 orbital. Since this orbital is strongly C⟷I anti-bonding, the transition may well cause dissociation of the molecule to $CH_3(^2A_1)$ and I(^2P). It may be formulated in C_{3v} symbols as

$$\cdots (ee)^3(a_1),\ {}^1E \longleftarrow \cdots (ee)^4,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or in diatomic molecule symbols as

$$\cdots (\Pi)^3(\bar{\sigma}),\ {}^1\pi \longleftarrow \cdots (\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where ($\bar{\sigma}$) stands for the anti-bonding orbital.

The next-lowest-energy transition should be of an electron from the I(5p)ee orbitals to the orbital symbolized as (2). This orbital also has its minimum on the 90° ordinate. In the upper state the HCH angle therefore decreases. As it does so, the upper orbital becomes more purely the I(6s)a_1 orbital. At the same time, it becomes less markedly C–I anti-bonding. The transition may therefore lead to a stable upper state. It may be formulated as (3) or, in diatomic molecule symbols, as

$$\cdots (5p\pi)^3(\mathrm{I}(6s)\sigma),\ {}^1\Pi \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This is an allowed transition giving rise to perpendicular bands. The upper state is degenerate. Only totally symmetrical vibrations are expected to appear strongly. Since the HCH angle in the equilibrium form of the upper state will be reduced relative to the ground state, one will expect the totally symmetrical hydrogen-bending frequency (ν_2a_1) to appear strongly in the absorption. Since the upper orbital should have some C⟷I anti-bonding character, the totally symmetrical C–I valence vibration (ν_3a_1) may also be expected to appear, though probably less strongly. Its frequency should be reduced in the upper state relatively to the lower.

The orbitals concerned in (5) are those of the iodine atom. For such a heavy atom, (J,j) rather than (Λ,S) coupling is expected (see Mulliken, *Phys. Reviews*, **1942**, **61**, 277). Transition (5) should therefore appear as the two transitions which may be formulated

$$\cdots (5p\pi)^3,\ {}^2\Pi_{\frac{1}{2}},\ (\mathrm{I}(6s)\sigma) \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad (5a)$$

and

$$\cdots (5p\pi)^3,\ {}^2\Pi_{1\frac{1}{2}},\ (\mathrm{I}(6s)\sigma) \longleftarrow \cdots (5p\pi)^4,\ {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad (5b)$$

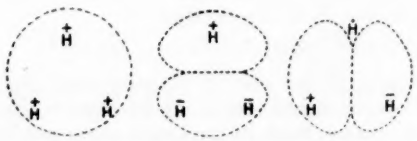
These two transitions should be separated by an amount closely similar to that of the doublet components of the CH_3I^+ ion, namely, by *ca.* 5060 cm.$^{-1}$ (Price, *J. Chem. Phys.*, 1936, **4**, 539). It is here that the main difference between the spectra of CH_3I and CH_3Br, CH_3Cl, and CH_3F will lie; for as we proceed from I to Br to Cl to F the coupling of the orbitals concerned in the transitions will become more and more (Λ,S) in type, *i.e.*, the separation of the transitions analogous to (5*a*) and (5*b*) will tend to the separation of upper $^3\Pi$ and $^1\Pi$ states (see Mulliken, *loc. cit.*).

We have still one further refinement to make. It is possible to think of H_3 in CH_3I as a group. The " valency " orbitals of this group are symbolized in Fig. 3. They comprise an a_1 orbital which may be written $H_1(1s) + H_2(1s) + H_3(1s)$ and two degenerate e orbitals which may be written $H_1(1s) - \frac{1}{2}[H_2(1s) + H_3(1s)]$ and $H_2(1s) - H_3(1s)$, together with the appropriate constants. (The choice of form for the degenerate orbitals is not unique.) The symmetry properties of these orbitals are the same as those of one nitrogen $2pa_1$ and two $2pe$ valency orbitals. In other words, the orbitals of CH_3I have a qualitative similarity to those of NCI. Now, by a simple extension of the arguments given in this paper and in Part II, it is readily shown that the NCI molecule should be bent in the excited state corresponding to (5), although linear in its ground state. It follows that in the equilibrium forms of the excited states of (5*a*) and (5*b*), the I atom should lie off the trigonal axis of the CH_3 group. The point is very similar to that made in Part VI, where

it was argued that in the first excited state of the CH_2O molecule the O atom might lie out of the mirror plane bisecting the HCH angle. The amount by which the I atom lies off the CH_3 symmetry axis will probably be small. The consequences of the deformation, however, should be at least three-fold. First, the rotational fine structure of the transitions (*5a*) and (*5b*) should be affected in certain ways. Secondly, the ν_6e vibration should appear in the transitions. Thirdly, the degeneracy of each of the upper states of (*5a*) and (*5b*) should be slightly split.

Observed Spectrum of CH_3I.—The longest-wave-length absorption region of methyl iodide has a maximum at about 2500 Å. In accord with our expectations it is continuous. It may confidently be assigned to the transition formulated as (3) or (4). There have been earlier suggestions that it includes a Rydberg transition. The low intensity makes this very unlikely and the matter is discussed elsewhere (Sutcliffe and Walsh, unpublished paper). The absorption of next longest wave-length consists of very similar band systems around 2000 and 1800 Å. The separation of the origins of the two systems is 4915 cm.$^{-1}$. They are the only systems which can represent the first ($n = 6$) members of a certain pair of Rydberg series found at shorter wave-lengths. These series are known to have upper orbitals that are (*ns*) iodine atomic orbitals and proceed to the doublet components of the molecular ion (Sutcliffe and Walsh, *loc. cit.*). The two band systems may therefore be

FIG. 3.



confidently assigned to transitions (*5a*) and (*5b*). The vibrational structure of the first of them is reproduced by Sponer and Teller (*Rev. Mod. Phys.*, 1941, **13**, 111). A striking feature of this structure is the appearance of the totally symmetrical ν_2a_1 CH_3 deformation vibration in both the ground and the upper state. The totally symmetrical C–I valence vibration (ν_3a_1) appears more weakly in both the ground and the upper state. Sponer and Teller comment : " These bands are due to an excitation of an iodine electron. It is therefore astonishing that the CH_3 vibration is more strongly excited than the C–I vibration." It is, however, a natural consequence of the arguments given above. In further accord with our expectations, the ν_6e vibration appears in both the ground and the upper state. The narrowness of the rotational fine structure of certain of the bands was at first thought to show that they represented parallel transitions. It was later concluded (Mulliken and Teller, *Phys. Review*, 1942, **61**, 283; Sponer and Teller, *loc. cit.*) that the electronic transition itself was perpendicular and led to a degenerate (Π) upper state for which the symmetrical configuration did not correspond to the equilibrium position. No trigonal axis of symmetry was present in the equilibrium form of the upper state, though the deviation from the three-fold axis was only slight. The narrow spacing of certain of the bands was due to the small additional electronic angular momentum resulting from this deviation. The slight splitting of the degeneracy of the upper states, due to the deviation, is observable, being $\simeq$50 cm.$^{-1}$ for the vibrationless bands; it is particularly well seen in the spectrum of CF_3I, which is very similar to that of CH_3I (Sutcliffe and Walsh, *loc. cit.*). A larger splitting occurs in the spectrum of ethyl iodide where the deviation from C_{3v} symmetry is of course marked even in the ground state (Sutcliffe and Walsh, *loc. cit.*).

The observations of, and deductions from, the spectra of CH_3I and related molecules are thus in complete accord with the theoretical expectations developed above.

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474. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part IX.* Hexatomic Molecules: Ethylene.*

By A. D. Walsh.

The electronic orbitals of the ethylene molecule are described. It is concluded that the first, triplet or singlet, excited state of the molecule should have (i) a pyramidal arrangement of the bonds about each C atom, (ii) one CH_2 group twisted relative to the other through 90° about the C–C bond, and (iii) each C atom possibly slightly out of the mirror plane that bisects the HCH angle of the other CH_2 group. The first excited state of a molecule containing n electrons should belong to the same symmetry class as the ground state of a similar molecule containing $n + 1$ or $n + 2$ electrons. The symmetry of the ground state of the N_2H_4 molecule affords strong support for conclusions (i) and (ii) concerning the first excited state of the C_2H_4 molecule.

Orbitals of C_2H_4.—The ethylene molecule in its ground state belongs to the symmetry class V_h. The definitions of the symbols appropriate to the orbitals of such a molecule are given in the Table below. yz is taken as the plane of the molecule, z being the long axis. $C_2(z)$ and $C_2(y)$ denote rotations of 180° about the z and the y axis respectively. $\sigma_v(z)$ and $\sigma_V(y)$ denote reflections in planes perpendicular to the z and the y axis respectively. i denotes the operation of inversion at the centre of symmetry.

Each CH_2 group, in symbols appropriate to its localized C_{2v} symmetry, will contain orbitals a_1, b_2 as for HCHO (see Part VI). Orbital a_1, having fewer nodal surfaces, is the more tightly bound. Considering non-localised orbitals, we obtain from the two a_1 orbitals new orbitals—one a sum and the other a difference. The new orbitals extend over the whole molecule and it is therefore appropriate to describe them by symbols of the V_h group. The first is bonding between the two CH_2 groups and is a_{1g} in type; the second is anti-bonding between the two CH_2 groups and is b_{1u} in type; both are bonding in all the C–H links.

Symbols used for molecular orbitals of V_h *molecules.*

Symbol	$C_2(z)$	$C_2(y)$	$\sigma_V(y)$	$\sigma_V(z)$	i	Symbol	$C_2(z)$	$C_2(y)$	$\sigma_V(y)$	$\sigma_V(z)$	i
a_{1g}	+	+	+	+	+	b_{2g}	−	+	+	−	+
a_{1u}	+	+	−	−	−	b_{2u}	−	+	−	+	−
b_{1g}	+	−	−	+	+	b_{3g}	−	−	−	−	+
b_{1u}	+	−	+	−	−	b_{3u}	−	−	+	+	−

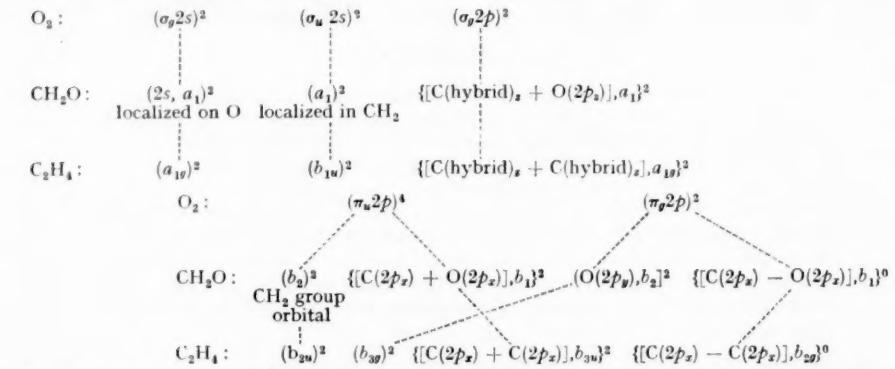
Fig. 1 shows the forms of the two b_2 orbitals. They give one non-localized orbital that is bonding between H_1 and H_3, H_2 and H_4, and another that is anti-bonding between H_1 and H_3, H_2 and H_4. Both are anti-bonding from H_1 to H_2 and from H_3 to H_4. The first is b_{2u} and the second b_{3g}. With respect to the symmetry of the whole molecule, the orbitals that are often loosely referred to as the "σ" and "π" orbitals of the C–C bond possess the labels a_{1g} and b_{3u} respectively. More explicitly, they might be symbolized $[C(\text{hybrid})_z + C(\text{hybrid})_z]$,$a_{1g}$ and $[C(2p_x) + C(2p_x)]$,b_{3u} respectively. The whole ground-state configuration of the C_2H_4 molecule may therefore be written

$$(a_{1g})^2(b_{1u})^2(a_{1g})^2(b_{2u})^2(b_{3g})^2(b_{3u})^2,\ {}^1A_{1g}$$

There is general agreement that the (b_{3u}) or "π" orbital is the most weakly bound orbital to be occupied in the ground state. An anti-bonding "π" orbital is also possible. It may be symbolized as $[C(2p)_z - C(2p)_z]$,b_{2g}. Just as we have seen (Part VI) that the experimental facts fit with the anti-bonding "π" orbital's being the lowest orbital unoccupied in the ground state of CH_2O, so we may expect the corresponding orbital to be the lowest orbital unoccupied in the ground state of C_2H_4.

* Part VIII, preceding paper.

It will be useful to formulate the symbols for corresponding orbitals of the isoelectronic O_2, CH_2O, and C_2H_4 molecules:


O₂ : (σg2s)² (σu 2s)² (σg2p)²
CH₂O : (2s, a₁)² localized on O (a₁)² localized in CH₂ {[C(hybrid)z + O(2pz)],a₁}²
C₂H₄ : (a1g)² (b1u)² {[C(hybrid)z + C(hybrid)z],a1g}²
O₂ : (πu2p)⁴ (πg2p)²
CH₂O : (b₂)² CH₂ group orbital {[C(2px) + O(2px)],b₁}² (O(2py),b₂]² {[C(2px) − O(2px)],b₁}⁰
C₂H₄ : (b2u)² (b3g)² {[C(2px) + C(2px)],b3u}² {[C(2px) − C(2px)],b2g}⁰

It will be seen that the degeneracies of the $(\pi_u 2p)$ and $(\pi_g 2p)$ orbitals are split in passing from O_2 to CH_2O. The indices refer to the number of electrons occupying the orbitals in the ground states. The energy order of the orbitals for O_2 is established. It is likely that the corresponding order is maintained in CH_2O and C_2H_4, except for the reversal of the two outermost orbitals occupied in the ground states of CH_2O and C_2H_4. This reversal is understandable in terms given below.

Just as we showed in Part VI that the anti-bonding " π " orbital in CH_2O had maximum binding energy when the HCH angle ($\doteqdot$ the HCO angle) was 90°, so it can be shown that the corresponding orbital in C_2H_4 has maximum binding energy when the HCH($\doteqdot$ the HCC angle) is 90°. It is sufficient to base our expectation, however, on the correspondence of the orbitals between the two isoelectronic molecules, and to conclude that the C_2H_4 transition

$$\cdots (b_{3u})(b_{2g}),\ {}^1B_{1u} \longleftarrow \cdots (b_{3u})^2,\ {}^1A_{1g} \quad . \ . \ . \ . \ . \ . \quad (1)$$

leads to an upper state that has a pyramidal arrangement of the bonds about each C atom. It is also possible (cf. CH_2O) that in the excited state each C atom will lie slightly out of the mirror plane of the other CH_2 group that is perpendicular to the plane of that CH_2 group.* These conclusions have not previously been realized. (1) is probably the lowest-energy singlet–singlet transition of the molecule.†

This does not suffice, however, to determine the shape of the excited C_2H_4 molecule. A further change of shape is possible with C_2H_4 that was impossible with CH_2O, namely, a twisting of the two CH_2 groups relative to each other about the C–C bond.

Twisting of the CH_2 *Groups about the* C–C *Bond.*—Consider first the O_2 molecule. The molecular-orbital explanation of why the ground state of the O_2 molecule is a triplet is simple and well-known. However, an equally simple explanation can be given as follows.‡ Suppose the molecule to be formed by the approach of two O atoms along the z direction. Suppose the configuration of each atom is

$$\cdots 2p_x\ 2p_y^2\ 2p_z$$

Then the $2p_z$ atomic orbitals overlap to form a σ bond, while the $2p_x$ atomic orbitals overlap to form a π bond. This means that, in addition, a $2p$ lone-pair of electrons is

* The explanation would be that excitation of an electron from the b_{3u} CC orbital results in the b_{2g} CH_2 group orbital being " pulled " away from the H atoms and more on to the C atoms, and that an occupied orbital that is largely built from in-plane $2p$ orbitals on the C atoms tends to cause in-plane bending of the molecule.

† Craig (*Proc. Roy. Soc.*, 1950, *A*, **200**, 272), however, considers the first singlet–singlet transition to be ${}^1A_{1g} \longleftarrow {}^1A_{1g}$, where the upper state arises by a *two*-electron jump to the (b_{2g}) orbital. Moffitt (*Proc. Phys. Soc.*, 1950, **63**, *A*, 585) has criticized this.

‡ This explanation should be used with care, especially when it is remembered that there is no practical distinction between the x- and the y-direction for a linear molecule. Nevertheless, the author believes it to be of value in giving a very simple way of gaining some insight into the fundamental reasons for the triplet ground state of O_2 and the shape of the H_2O_2 molecule, their connection with the low height and twisted nature of the C_2H_4 lowest triplet state, and several facts concerning the CH_2O molecule.

present on each atom, these electrons being in orbitals pointing in the same direction. Lone pair–lone pair repulsion is thus present. The repulsion arises from four electrons trying to occupy the same orbital in the region of overlap. By the Pauli principle, they cannot do this. The difficulty can be avoided either by supposing that the two pairs of electrons repel each other, so that their orbitals do *not* overlap, or by constructing *two* new molecular orbitals (one bonding and one anti-bonding). The second alternative is adopted in the most usual orbital theory. The first is adopted here and its possibilities explored. Lone pair–lone pair repulsion is a language used, *e.g.*, by Walsh (*J.*, 1948, 398) to express an effect that, on more usual theory, would be described by saying that excitation of electrons to anti-bonding molecular orbitals occurs.

Of course, there is no actual distinction of the x and the y direction for a linear molecule, so that the proper wave functions would be combinations of those built as above and those in which the x and y suffixes were interchanged; but we can still conceive of a state of the O_2 molecule in which all electrons are paired and wherein occur

$$\text{A } \sigma \text{ bond} + \text{a } \pi \text{ bond} + \text{lone pair–lone pair repulsion} \quad . \quad . \quad . \quad (2)$$

The repulsion could be avoided if, as the two atoms approached, their configurations were supposed to be twisted with respect to each other so that one obtained

$$\text{A } \sigma \text{ bond} + \underbrace{\text{interaction of odd electron and lone pair}}_{\text{in orbitals "pointing" in the } x \text{ direction}} + \underbrace{\text{interaction of odd electron and lone pair}}_{\text{in orbitals "pointing" in the } y \text{ direction}} \quad . \quad . \quad . \quad . \quad (3)$$

The latter two interactions could be called "three-electron bonds." There is empirical evidence that such interactions are attractive, with a strength about one-half of that of the corresponding single bond. Theoretically, this is most simply seen by reverting for a moment to the usual orbital language and noting that two electrons would occupy the bonding $\psi_1(2p) + \psi_2(2p)$ orbital and one the corresponding anti-bonding $\psi_1(2p) - \psi_2(2p)$ orbital, giving a net effect of approximately half a filled bonding orbital. Expression (3) may thus be re-written as

$$\text{A } \sigma \text{ bond} + \sim \tfrac{1}{2} \text{ a } \pi \text{ bond} + \sim \tfrac{1}{2} \text{ a } \pi \text{ bond}$$

or

$$\text{a } \sigma \text{ bond} + \sim \text{a } \pi \text{ bond} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

but without any repulsion effect. Comparing this with (2), one sees that it is probable that the state of the O_2 molecule reached by the second mode of interaction of two O atoms lies lower in energy than the state reached by the first mode of interaction. One can therefore understand why the ground state of the O_2 molecule should contain two unpaired electrons. The essential reason may be thought of as the twisting of one O atom configuration relatively to the other to eliminate the lone pair–lone pair repulsion that would otherwise be present.

Such an account at once explains why the ground state of the H_2O_2 molecule should be skew and not planar. One H atom pairs with the odd "$2p_x$" electron and the other with the odd "$2p_y$" electron of the O_2 ground state.

Consider now the C_2H_4 molecule. A CH_2 group is isoelectronic with an O atom and, as we have seen, the orbitals of C_2H_4 correspond to those of O_2. In particular, the b_2 CH_2 group orbitals correspond to the $2p\pi$ O orbitals of the O_2 molecule. The electrons in the filled b_2 CH_2 group orbitals must repel each other in the C–C bond of C_2H_4, just as the electrons in the filled, parallel, $2p\pi$ atomic orbitals repel each other in the O–O bond of singlet O_2. This repulsion is described in alternative language by saying that two electrons occupy the $CH_2 \longleftrightarrow CH_2$ anti-bonding (b_{3g}) molecular orbital. On the other hand, the repelling b_2 CH_2 group electrons are further apart (see Fig. 1) than would be repelling O $2p\pi$ electrons. The repulsion in the ground state of the C_2H_4 molecule, analogous to the lone pair–lone pair repulsion of the O_2 molecule, will therefore be comparatively weak and it is not surprising that the ground state of C_2H_4, unlike that of O_2, is singlet. The magnitude of the repulsion will be indicated by the energy needed to raise the C_2H_4

molecule to a triplet state analogous to $O_2\ ^3\Sigma_g^-$. Estimates of this energy vary, but there is general agreement that the C_2H_4 molecule does have a comparatively low-lying triplet state. The reason for the low height can be thought of as the tendency of the two CH_2 groups to twist relatively to each other in order to remove the analogue of the lone pair–lone pair repulsion existing in, for example, the $O_2\ ^1\Delta_g$ or $^1\Sigma_g^+$ state. In the ground state the tendency to twist is opposed by the tendency of the " π " C–C bond to keep the two CH_2 planes identical. In the upper state of transition (1), however, this opposition is partly removed, the effect of the anti-bonding (b_{2g}) electron roughly cancelling that of the bonding b_{3u} electron. One deduces that the excited state (other geometrical changes being for the moment neglected) will be most stable when the planes of the two CH_2 groups are at 90°.

Olson (*Trans. Faraday Soc.*, 1931, **27**, 69) first suggested that the C_2H_4 absorption near 2000 Å involved an upper state of this shape. The conclusion has been deduced theoretically, in language less simple than that used here, by Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 265) and by Mulliken and Roothaan (*Chem. Reviews*, 1947, **41**, 219). Mulliken called the $CH_2 \longleftrightarrow CH_2$ repulsion that is responsible " second-order hyperconjugation."

The CH_2O molecule must be even closer than C_2H_4 to O_2 in electronic structure. The analogue of the lone pair–lone pair repulsion will now be between the electrons in the CH_2 b_2 group orbital and those in the $O(2p_y)$,b_2 lone-pair orbital. It will be stronger than the corresponding repulsion in C_2H_4. Various consequences of this may be traced in the facts relating to the CH_2O molecule. For the present we note that it explains the reversal in the energy order of the two outermost orbitals occupied in the ground states of CH_2O

FIG. 1.

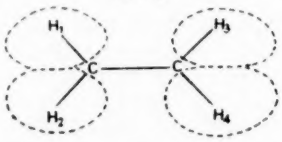


FIG. 2.

and C_2H_4. Because the lone pair–lone pair repulsion, which makes the ($\pi_g 2p$) orbital of O_2 and the corresponding $O(2p_y)$,b_2 orbital of CH_2O lie high in energy, is much weaker in C_2H_4, the corresponding (b_{3g}) orbital of C_2H_4 will be more tightly bound relatively to the other C_2H_4 orbitals.

Shape of the First Excited State of C_2H_4 : *Evidence.*—The conclusion reached above is that in its first excited state (either singlet or triplet) the C_2H_4 molecule should have (i) one CH_2 group twisted though 90° relative to the other, (ii) a pyramidal arrangement of the bonds about each C atom, and (iii) each C atom possibly slightly out of the mirror plane bisecting the HCH angle of the other CH_2 group. That at least the first two of these conclusions are correct can be strongly supported as follows. A corollary of the molecular-orbital approach adopted in this series of papers is that the symmetry of the first excited state of a molecule containing n electrons should be the same as that of the ground state of the similar molecule containing $n + 1$ or $n + 2$ electrons. The latter, in relation to the ground state symmetry of the molecule containing n electrons, reveals how the first excited orbital of the latter tends to stabilize the molecule, a tendency possibly all the greater in the first excited state of the n-electron molecule because one electron may then be missing from an orbital tending to stabilize the molecule in its original shape. As examples of the corollary, the first excited state of CO_2 should belong to the same symmetry class as the ground states of NO_2 and SO_2; the first excited state of NO_3^- should have the same symmetry as the ground state of NF_3; and the first excited state of CH_2O should be similar to the ground state of H_2NF. We can therefore test our conclusions as to the symmetry of the first excited state of C_2H_4 by means of the shape of the ground state of the hydrazine molecule. Scott, Oliver, Gross, Hubbard, and Huffman (*J. Amer. Chem. Soc.*, 1949, **71**, 2293; see also Wagner and Bulgozdy, *J. Chem. Phys.*, 1951, **19**, 1210, and Giguère and Liu, *ibid.*, 1952, **20**, 136), from the evidence of infra-red spectroscopy concluded that the molecule has a pyramidal arrangement of the bonds about each N atom, a staggered

configuration of the H atoms (somewhat as Fig. 2) being favoured. Collin and Lipscomb (*Acta Cryst.*, 1951, **4**, 10) suggest that in the crystal the H atoms lie in the opposed or eclipsed configuration. However, the barrier to rotation about the N–N bond should be small, so that crystal forces might cause the eclipsed form to be more stable in the solid state, even though the staggered configuration is the more stable in the isolated molecule. The configuration favoured by Scott *et al.* is just that expected for the first excited state of C_2H_4 on the basis of (i) and (ii) above. There appears to be no evidence to support expectation (iii), but the deviation may be so small as not to be easily detected.

Vibrational Structure to be expected for the First Transition of C_2H_4.—In the light of our expectations as to the shape of the $^1B_{1u}$ state of C_2H_4, at least the following vibrations might be expected to appear in the transition (1) or its triplet←singlet analogue: (i) the C–C valence vibration, $\nu_2 a_g$, which has a frequency 1623 cm.$^{-1}$ in the ground state; (ii) the CH_2–CH_2 twisting vibration, $\nu_4 a_u$, which has a frequency 1027 cm.$^{-1}$ in the ground state (Arnett and Crawford, *J. Chem. Phys.*, 1950, **18**, 118); (iii) one or both of the out-of-plane bending vibrations, $\nu_7 b_{1u}$ and $\nu_8 b_{2g}$, which have frequencies 949 and 943 cm.$^{-1}$ respectively in the ground state (these are included because of the tendency of the C atoms to assume a pyramidal bond arrangement); (iv) one or both of the in-plane deformation vibrations, $\nu_{10} b_{2u}$ and $\nu_6 b_{1g}$, which have frequencies 995 and 1050(?) cm.$^{-1}$ respectively in the ground state (these may be thought of as arising from the rotation of the two CH_2 groups about axes perpendicular to the molecular plane, and are included because of the expectation that each C atom may lie out of the mirror plane bisecting the HCH angle of the other CH_2 group). In addition, the following might also occur: (v) one or both of the CH_2 deformation vibrations ν_3 and ν_{12} which change the HCH angles relatively to the HCC angles [they are included because it is improbable that in the excited state angle HCH remains approximately equal to angle HCC (cf. Part VIII)]; (vi) one or both of the CH stretching vibrations ν_1 and ν_{11} (these are included because the change of bond arrangement from planar to pyramidal implies that the C valencies towards the H atoms, and hence the C–H stretching force constants change).

If, as is probable from the arguments above, the upper state departs appreciably from V_h symmetry, the symbol B_{1u} is not strictly applicable and any symmetry restrictions on which vibrations can occur are relaxed. Unfortunately, the absorption that is best identified as transition (1) is continuous, having a maximum at *ca.* 1615 Å. It is difficult therefore to test our expectations. A system of bands observed by Snow and Allsopp (*Trans. Faraday Soc.*, 1934, **30**, 93) in the range 1935—2069 Å and yielding a frequency between 760 and 920 cm.$^{-1}$ may either represent the tail of the 1615-Å absorption or the $^1A_{1g} \leftarrow\!\!- {}^1A_{1g}$ transition suggested by Craig or part of the triplet←singlet analogue of (1) (Moffitt, *loc. cit.*). In the second of these possibilities the system is due to a two-electron jump between the same two orbitals as the one-electron jump (1). In any case, therefore, the frequencies involved are likely to represent one or more of the vibrations (i)—(iv).—The biggest changes of geometry in the equilibrium form of the upper state are probably the lengthening of, and twisting about, the C–C bond. Vibrations (i) and (ii) are perhaps therefore likely to be the most prominent. It is noteworthy that Reid (*J. Chem. Phys.*, 1950, **18**, 1299) has observed a system of weak absorption bands in the near ultra-violet which is plausibly supposed to represent the triplet–singlet analogue of (1), and has attributed the band separation of 995 cm.$^{-1}$ to the upper-state twisting frequency. It is also noteworthy that the first known absorption of *cyclo*pentene (Carr and Stuecklen, *ibid.*, 1938, **6**, 55) shows a long succession of narrow shallow bonds which have separations of 90—160 cm.$^{-1}$ and are believed to represent puckering vibrations of the ring, which are to be expected on the basis of expectations (i)—(iv) above.

The list of possible C_2H_4 vibrations that might appear in its spectrum is a formidable one and there is little direct evidence in favour of most of the possibilities. Nevertheless, indirect support for the ideas on which the list is based is to be found in the spectrum of benzene which is briefly dealt with in the following paper.

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475. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part X.* A Note on the Spectrum of Benzene.*

By A. D. Walsh.

The reasons are discussed for the appearance of numerous non-totally symmetrical vibration frequencies in the near-ultra-violet spectrum of benzene. On the basis of conclusions reached in Part IX * and on the assumption that changes of restoring forces in the first excited states of benzene relatively to the ground state are similar to those in the first excited state of ethylene relatively to its ground state, a large number of such vibrational modes might be expected in the benzene spectrum.

There has been much study of the first singlet–singlet absorption and fluorescence transitions of benzene (see, especially, Garforth, Ingold, and Poole, *J.*, 1948, 406). As a result, the vibrational structure is now well-established and it is generally accepted that (*a*) the transition is an electronically forbidden one, (*b*) the upper state is either $^1B_{2u}$ or $^1B_{1u}$, (*c*) the transition is made allowed by an e_g^+ vibration. There has also been a vibrational analysis of the first triplet→singlet emission spectrum (Shull, *J. Chem. Phys.*, 1949, **17**, 295). The upper state in this emission is either $^3B_{1u}$ or $^3B_{2u}$. In these spectra progressions occur in the totally symmetrical, breathing, vibration of the hexagon. The occurrence of these progressions is explained as due to an expansion of the hexagon in the upper state (Garforth, Ingold, and Poole, *J.*, 1948, 508; Craig, *J.*, 1950, 2146). Numerous other vibrations appear in the spectra; but hitherto there appears to have been no attempt to explain *why* they appear. The fact that one of them (*e.g.*, an e_g^+ vibration for the singlet–singlet transition) enables the electronically forbidden transition to appear is of course no explanation of why it appears.

The fundamental reason for the appearence of these vibrations must be that they occur in response to a change in restoring forces consequent upon the electronic excitation. Alternatively, they may be supposed to occur in response to a change of geometry in the equilibrium form of the upper state relatively to the ground state; but if this viewpoint is adopted then the departure from D_{6h} symmetry in the upper state must be supposed sufficiently small for classification of the levels according to the symmetry operations appropriate to the D_{6h} class to retain its importance.† The situation is very like that in the near-ultra-violet absorption of formaldehyde (Part VI, *J.*, 1953, 2306) where the conclusion was reached that the upper state had a shape sufficiently different from that of the ground state to cause the appearance of certain vibrations, but sufficiently close to C_{2v} symmetry for formulations in terms of symbols appropriate to the latter symmetry to remain important.

In Part IX we concluded that, in the first excited state of the C_2H_4 molecule, (i) the C–C bond should be lengthened, (ii) the $-C\lesssim$ groups should be twisted relatively to each other, (iii) each C atom should probably move out of the mirror plane bisecting the HCH angle of the other CH_2 group, and (iv) the arrangement of the three bonds about each C atom should become pyramidal; and probably (v) the CH bonds should lengthen and (vi) the angles between the three bonds attached to either C atom should not remain equal. Conclusion (iii) may be thought of as a tendency of the $-C\lesssim$ groups to rotate about axes perpendicular to their planes. The fundamental hypothesis of the present paper is that tendencies to change of length and arrangement of the bonds about any C atom should be present in the first excited states of benzene similar to those in the first excited state of ethylene. The excited orbital in the $^{3,1}B_{1u}$, the $^{3,1}B_{2u}$, and the $^1E_u^-$ states mentioned here is similar in certain respects to that of the first excited state of ethylene.

* Part IX, preceding paper.

† Change of shape of the benzene molecule on excitation should be much less than the change of shape of the ethylene molecule on similar excitation because (*a*) in benzene only one "π"-electron out of six is excited compared with one of two for ethylene and (*b*) the ring form of the benzene molecule restricts, *e.g.*, twisting of the bonds.

The vibration forms of the benzene molecule are conveniently given by Bailey, Ingold, Poole, and Wilson (*J.*, 1946, 231). Because of (i), we expect the a_{1g}(C) vibration to appear. Because of (v), we expect the a_{1g}(H) vibrations to appear. By making a model in which the arrangement of bonds about any C atom is pyramidal and applying twists to the various C–C links, it is possible to achieve forms which would be reached during the a_{2u}, b_{2g}(C), b_{2g}(H), e_u^+(C), e_u^+(H), and e_g^- vibrations. In other words, because of (ii) and (iv), we expect each of the out-of-plane deformation vibrations of the benzene molecule possibly to appear. Because of (iii), (v), and (vi), we expect in-plane deformation vibrations to appear, *e.g.*, the four e_g^+ modes.

A large number of the possible vibrations of the benzene molecule may therefore appear. This is in accord with the analyses of the spectra that have been carried out. In the first singlet–singlet absorption, for example, the following vibrations have all been identified (Garforth and Ingold, *J.*, 1948, 420): a_{1g}(C), a_{1g}(H), a_{2u}(H), b_{2g}(C), b_{2g}(H), e_g^+(C1), e_g^+(C2), e_g^+(H1), e_u^+(C), e_u^+(H), and e_g^-(H). The e_g^+(H2) vibration appears in the triplet–singlet emission. Which of these vibrations will be particularly prominent or what changes in quantum number may occur for a particular vibration will of course be determined largely by the symmetry of the upper level. Thus at least one e_g^+ vibration is expected to be prominent for a $^{e1}B_{1u}$ or $^{e1}B_{2u}$ upper state in order that the transition may perturb the nearest electronically allowed transition ($^1E_u^- \leftarrow\!\!- {}^1A_{1g}$); and at least one e_g^+, b_{2g}, or e_g^- vibration is expected to be prominent for a $^{e3}B_{1u}$ or $^{e3}B_{2u}$ upper state for a similar reason (see Craig, *J. Chem. Phys.*, 1950, **18**, 236). The prominence or otherwise of particular vibrations will also be affected by the exact geometry of the upper state and by the Boltzmann factors for bands originating from vibrating ground states; all the present paper does is to point out that the occurrence of so many vibrational modes is to be expected from the conclusions concerning the shapes of excited molecules reached in earlier papers of this series.

The argument may be reversed: the appearance of all the above vibrations may be taken as evidence for the conclusions of Part IX concerning the changes of shape or the restoring forces controlling the length and arrangement of the bonds about each C atom, in the first excited state of the C_2H_4 molecule relatively to its ground state.

Finally, it is interesting to trace the fundamental reasons for the occurrence of, *e.g.*, the e_g^+ and b_{2g} vibrations. The former occurs for essentially the same reason as the $\nu_6 e$ vibration occurs in the spectrum of methyl iodide or the $\nu_5 b_2$ vibration probably occurs in the spectrum of formaldehyde. This reason can be traced back first to the expectation that a $=C<$ group or a $-C\lessgtr$ group will resemble in certain respects an $O=C=$ or $N\equiv C-$ group respectively; then to the expectation that the CO_2 and the HCN molecule are bent in their first excited states; next to the expectation that a 4-electron AH_2 molecule is linear but a 5-electron AH_2 molecule bent; and in the last resort to the linkage of the shape of such a molecule with hybridization of the valencies of the central atom and the linkage of valency hybridization with bond strengths and the total potential energy of the molecule. The b_{2g} vibration occurs for essentially the same reason as the $\nu_2 a_1$ vibration occurs in the spectrum of methyl iodide or the $\nu_6 b_1$ vibration in the spectrum of formaldehyde; this reason can also be traced back through the successive papers of this series to the properties of the $a_1 s$–π_u and a_1–σ_g, b_2–σ_u orbitals described in Part I. Put in another way, the fundamental reason for occurrence of these vibrations lies in the need of a molecule to form the strongest possible bonds and yet to keep its *total* potential energy as low as possible. Because of the interactions between electrons these two needs often oppose one another. These considerations should make it clear that attempts to understand the benzene spectrum on the basis of changes in an isolated set of six " π "-electrons are inadequate; one has to consider interactions of all the electrons in the molecule.

LEEDS UNIVERSITY. [*Received, June 3rd*, 1952.]

476. *The Structure of Karaya Gum* (Cochlospermum gossypium).

By E. L. Hirst and Sonia Dunstan.

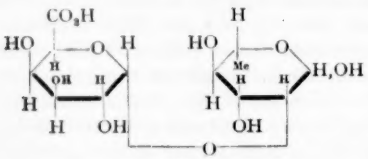
Karaya gum, from *Cochlospermum gossypium*, is a partly acetylated acidic polysaccharide, which gives on hydrolysis equimolecular proportions of L-rhamnose, D-galactose, and D-galacturonic acid, together with traces of a ketohexose. On partial hydrolysis, it gives rhamnose, galactose, galacturonic acid, 2-D-galacturonosyl-L-rhamnose, and 4-D-galacturonosyl-D-galactose, together with unidentified oligosaccharides of high uronic acid content.

Methylated karaya gum gives on hydrolysis 2 : 3 : 4-trimethyl (1 part), 3 : 4-dimethyl (1 part), and 3-methyl rhamnose (1 part), 2 : 3 : 4 : 6-tetramethyl (2 parts), 2 : 3 : 6-trimethyl (1 part), and 2 : 6-dimethyl galactose (*ca.* 1%), and a mixture of methylated uronic acids.

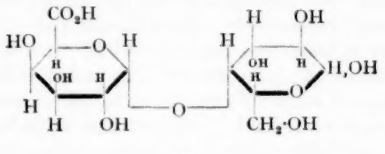
The oxidation of the deacetylated polysaccharide with periodic acid has been studied.

These investigations were carried out on a variety of karaya gum occurring as an exudate from the bark of *Cochlospermum gossypium* (family Bixineae), a small deciduous tree which grows in the forests of the North-West Himalaya. An exudate from *Sterculia urens* has also been termed karaya gum and a preliminary investigation of the gum from *S. urens* (Hough and Jones, unpublished results) has shown that the two gums are closely alike. This applies also to other gums from trees of the Sterculiaceae family, namely, *S. tormentosa* (Beauquesne, *Compt. rend.*, 1946, **222**, 1056) and *S. setigera* (Hirst, Hough, and Jones, *J.*, 1949, 3145), and is borne out by the acetyl content (18·9%), the high proportion of uronic acid residues, and the occurrence of residues of L-rhamnose, D-galactose, D-galacturonic acid, and a ketohexose. Two of these gums, namely, those from *S. setigera* and *S. urens*, have given D-tagatose on hydrolysis (see Hirst, Hough, and Jones, *loc. cit.*).

Cochlospermum gossypium gum, which will be referred to as karaya gum, swells in water to a bulky gel. Purification was effected by precipitation by alcohol from acidified aqueous solutions, the ash-free gum being a white, amorphous, hygroscopic powder. After hydrolysis by aqueous acid and separation of the products into neutral and acid fractions, it was found that L-rhamnose, D-galactose, and D-galacturonic acid were present in equimolecular proportions, together with a trace of a labile ketohexose. It is likely that most of this ketose is destroyed even under mild conditions of hydrolysis.



(I)



(II)

Partial hydrolysis of the gum gave a mixture of monosaccharides and acidic oligosaccharides. After methylation of the latter followed by distillation of the product, fractions were obtained which yielded on hydrolysis 3 : 4-dimethyl L-rhamnose, 2 : 3 : 6-trimethyl D-galactose, and 2 : 3 : 4-trimethyl D-galacturonic acid. Traces of lower methylated derivatives were also present. These observations indicate that the oligosaccharides obtained by this partial hydrolysis of karaya gum were mainly 2-D-galacturonosyl-L-rhamnose (I) and 4-D-galacturonosyl-D-galactose (II).

The gum was converted into its fully methylated derivative, which appeared to be substantially homogeneous. Hydrolysis with formic acid then gave a complex mixture of neutral methylated reducing sugars and methylated uronic acids. Examination of the neutral fraction by paper partition chromatography revealed six spots, corresponding to 2 : 3 : 4-trimethyl rhamnose, 2 : 3 : 4 : 6-tetramethyl galactose, 3 : 4-dimethyl rhamnose, 2 : 3 : 6-trimethyl galactose, a crystalline monomethyl rhamnose, and 2 : 6-dimethyl

galactose (see Table, p. 2336). The mixture of methylated sugars was separated into eight fractions by partition chromatography on a column of cellulose with light petroleum–butanol saturated with water as mobile phase.

The monomethyl rhamnose was chromatographically different from 4-methyl rhamnose. Its methylglycoside did not reduce potassium periodate. Although too much significance cannot be attached to the results of such oxidations when applied to methylated sugars (Greville and Northcote, *J.*, 1952, 1945), the total lack of periodate consumption suggests the location of the methyl group at $C_{(3)}$, since in the event of two contiguous hydroxyl groups, at $C_{(2)}$ and $C_{(3)}$, or $C_{(3)}$ and $C_{(4)}$, some oxidation might be expected, however incomplete.

Examination of the mixture of methylated uronic acids by paper partition chromatography revealed four spots, three cerise and one brown, on spraying with aniline oxalate. The mixture was separated into four fractions by partition chromatography on a column of celluose with butanol–glacial acetic acid saturated with water as mobile phase. The nature of these methylated uronic acids could not be ascertained with certainty but the second fraction appeared to consist of dimethyl galacturonic acids. The absence of any downward shift in optical rotation in cold methanolic hydrogen chloride indicates the absence of a free hydroxyl group on $C_{(4)}$, and suggests that this material was 2 : 4- or 3 : 4-dimethyl galacturonic acid or a mixture of the two.

On the basis of the evidence obtained it is possible to put forward the following figures as an estimate of the proportions of sugar derivatives formed on hydrolysis of methylated karaya gum: 2 : 3 : 4-trimethyl L-rhamnose (1 part), 2 : 3 : 4 : 6-tetramethyl D-galactose (2 parts), 3 : 4-dimethyl L-rhamnose (1 part), 2 : 3 : 6-trimethyl D-galactose (1 part), 3-methyl L-rhamnose (1 part), 2 : 6-dimethyl D-galactose (*ca.* 1%), and a mixture of methylated uronic acids the identity of which is still unresolved.

The deacetylated polysaccharide, on oxidation with potassium periodate, gave one mole of formic acid per 225 g. of gum, the reaction being complete in two days. This amount is in excess of that which would be liberated by the end groups known to be present in the gum and may be attributable to the oxidative degradation of uronic acid residues (Halsall, Hirst, and Jones, *J.*, 1947, 1427). On hydrolysis at this stage, the polysaccharide gave rhamnose (10·2%) and galactose (7·5%). It is not certain that this proportion of rhamnose and galactose gives an accurate representation of portions resistant to oxidation, since on oxidation for a further seven days the molecular proportion of galactose to rhamnose had decreased from 0·75 to 0·17. It is known that some methylated sugars are slowly and incompletely attacked by unbuffered periodate (Greville and Northcote, *loc. cit.*) and it is possible that the decreasing proportion of galactose as oxidation proceeds is due to a similar slow attack by the periodate.

At this stage it is not possible to formulate a unique molecular structure for the gum. The monomethyl rhamnose and monomethyl galacturonic acid, isolated from the hydrolysate of the methylated polysaccharide, must have arisen from residues which were triply-linked in the gum. It is clear, therefore, that the gum possesses a highly-branched structure. The small amount of dimethyl galactose, which may have arisen from incomplete methylation of the polysaccharide or from demethylation occurring during hydrolysis, scarcely influences the result as regards the main structural features.

Sugar residues, the presence of which has been definitely established, are as follows: Gal*p* 1 . . .,. . . 4 Gal*p* 1 . . ., Rha*p* 1 . . .,. . . 2 Rha*p* 1 . . .,. . . $\begin{matrix}4\ \text{Rha}p\ 1\\2\ \ \ \ \ \ \end{matrix}$ (Gal*p* = D-galactopyranose, Rha*p* = L-rhamnopyranose). Evidence from the isolation of acidic disaccharides by partial hydrolysis of the gum indicates that the residues Gal*p*A 1——2 Rha*p* and Gal*p*A 1——4 Gal*p* are also structural features of the molecule. The main linkages of the D-galacturonic acid residues appear to be of the types . . . *x* Gal*p*A 1 . . . ($x = 2$ or 3) and $\begin{matrix}\cdot\ \cdot\ \cdot\ x\\ \ \ \ \ \ \ y\end{matrix}$ Gal*p*A 1 . . . where *y* is unknown (Gal*p*A = D-galactopyranuronic acid).

The increase in the proportion of uronic acid residues after methylation (constituting one-half of the methylated polysaccharides, compared with one-third of the unmethylated material) may be due to a weakness in the glycosidic linkage of the ketose residues, with

the result that parts of the molecule are broken off during the reaction. It is to be remembered also that the location of the acetyl groups and their function in the molecular chain are as yet unexplored.

Experimental

B. p. recorded are bath-temperatures; optical rotations are measured in aqueous solution; solutions were evaporated under reduced pressure unless otherwise stated. Chromatography was carried out, unless otherwise stated, on Whatman No. 1 filter paper with butanol–ethanol saturated with water containing a little ammonia as mobile phase for neutral sugars, and with butanol–glacial acetic acid saturated with water in the case of uronic acids. R_G values are rates relative to that of tetramethyl glucopyranose.

Purification and Properties of Karaya Gum.—The gum from *Cochlospermum gossypium* occurs as the partly acetylated derivative of the inorganic salt of an acidic polysaccharide (Found : OAc, 18·9%). The gum was purified in the following way. The nodules were dried *in vacuo* at 100° over silica gel and were ground to a coarse powder which was slowly stirred into hot water. The resulting gel was heated with 5% aqueous sodium hydroxide at 60° for 24 hr. The opalescent orange solution was acidified with hydrochloric acid and filtered. The filtrate was poured, with stirring, into alcohol (4 vols.), the gum being precipitated as a white fibrous mass, which was triturated with alcohol until free from chloride ions, washed with methyl alcohol, then with ether, and dried *in vacuo* at 40°, giving a white powder, $[\alpha]_D^{20}$ +64° (*c* 4·0 in N-NaOH) [Found : C, 39·6; H, 7·6; ash, 0·61%; N, nil; S, nil; halogen, nil; equiv., 470 (by titration); furfuraldehyde, liberated by boiling hydrochloric acid, equiv. to 14·8% pentosan content]. The sodium salt of the gum was non-reducing and with copper sulphate gave an insoluble copper salt. The homogeneity of the gum was established by purifying each of four nodules *via* the insoluble copper salt. The properties of the purified samples were substantially the same.

Hydrolysis of the Acidic Polysaccharide.—The purified polysaccharide (2·32 g.) was hydrolysed with boiling N-sulphuric acid for 18 hr. The solution was neutralised with barium carbonate, filtered, and evaporated to a brown solid, which was extracted with boiling anhydrous methyl alcohol. The extracts were evaporated to a syrup (1·31 g.), which was dissolved in water. Barium ions were removed by sulphuric acid, and the filtrate evaporated to a syrup (0·70 g.). Paper chromatographic analysis showed the presence of rhamnose and galactose on spraying with aniline oxalate, and of a trace of ketose on spraying with urea hydrochloride. Estimation by periodate oxidation showed the presence of equimolecular proportions of rhamnose and galactose.

A large-scale hydrolysis of the purified polysaccharide (10 g.) resulted in the isolation of pure crystalline samples of D-galactose and L-rhamnose. D-Galactose {m. p. 160—162°; $[\alpha]_D^{18}$ +78·4° (*c*, 4·0)} was further characterised as its methylphenylhydrazone and by conversion into mucic acid. L-Rhamnose {m. p. 90—92·5°; $[\alpha]_D^{19}$ +8·0° (*c*, 2·0)} was characterised as its benzoylhydrazone, and its identity was confirmed by an *X*-ray powder photograph. The uronic acid was identified as D-galacturonic acid by oxidation to mucic acid and also by conversion in boiling 1% methanolic hydrogen chloride into the methyl ester of α-methyl-D-galacturonoside, m. p. 140°; $[\alpha]_D$ +124·0° (*c*, 0·5).

Methylation of Degraded Karaya Gum.—The purified polysaccharide (27 g.) was hydrolysed with boiling N-sulphuric acid until the optical rotation reached the maximum value ($[\alpha]_D$ +80·5° after 1 hr.). The solution was neutralised with barium carbonate and evaporated to dryness, and the neutral reducing sugars were removed by extraction with boiling methyl alcohol. The residual barium salts were purified by precipitation from aqueous solution by methyl alcohol. They were methylated three times with methyl sulphate and 30% sodium hydroxide solution (yield, 7·45 g.; OMe, 36·6%) and once with Purdie's reagents, giving a yellow syrup (6·48 g.; n_D^{19} 1·4667; OMe, 48·9%), which was fractionally distilled at 10^{-2} mm., giving fractions (i) a mobile liquid (1·07 g.), b. p. 144—170°, n_D^{18} 1·4487 (OMe, 50·2%; equiv., 267), (ii) a mobile liquid (0·49 g.), b. p. 170—174°, n_D^{18} 1·4546 (OMe, 50·3%; equiv., 264) (these two consisted almost entirely of methylated galacturonic acid and were discarded), (iii) a viscous syrup (0·99 g.), b. p. 225—240°, n_D^{18} 1·4678, $[\alpha]_D^{15}$ +73° (*c*, 1·9 in MeOH) (OMe, 47·9%; equiv., 354), and (iv) a semi-solid (1·67 g.), b. p. *ca.* 300°, n_D^{18} 1·4808, $[\alpha]_D^{15}$ +60° (*c*, 2·5 in MeOH) (OMe, 44·8%; equiv., 240). Fractions (iii) and (iv) were boiled with 7% aqueous hydrochloric acid. The products, separated into neutral sugars and the barium salts of the uronic acids, were worked up in the usual way. The barium salts were then converted into the free acids. Fraction (iii) was

shown by paper chromatography to be mainly 2 : 3 : 4-trimethyl galacturonic acid (R_G 0·65), and fraction (iv) contained also dimethyl galacturonic acid (R_G 0·47). Traces of lower methylated derivatives were also present. The free sugars from fractions (iii) and (iv) gave similar patterns of four spots when examined chromatographically: R_G 0·82 (3 : 4-dimethyl rhamnose), 0·70 (2 : 3 : 6-trimethyl galactose), 0·55 (monomethyl rhamnose, trace), and 0·43 (2 : 6-dimethyl galactose, trace). The intensities of the spots showed that the bulk of the material consisted of 3 : 4-dimethyl rhamnose and 2 : 3 : 6-trimethyl galactose. The experiment was then repeated on a larger scale, the neutral methylated sugars being separated by partition chromatography on a cellulose column with light petroleum (b. p. 100—120°; 3 vols.) and *n*-butanol (2 vols.) as mobile phase. Two main fractions were obtained: (*a*) 3 : 4-dimethyl L-rhamnose, identified as 3 : 4-dimethyl δ-L-rhamnonolactone, m. p. 76°, $[\alpha]_D^{20}$ −152° (*c*, 0·5), and as 3 : 4-dimethyl L-rhamnonamide, m. p. and mixed m. p. 154—156°, not depressed on admixture with an authentic sample, and (*b*) 2 : 3 : 6-trimethyl D-galactose, identified as 2 : 3 : 6-trimethyl γ-D-galactonolactone, m. p. and mixed m. p. 99°. The amounts of (*a*) and (*b*) separated were in the ratio 2 : 1. The main component of the methylated uronic acid fraction was 2 : 3 : 4-trimethyl D-galacturonic acid, identified after oxidation and esterification as dimethyl 2 : 3 : 4-trimethyl mucate, m. p. and mixed m. p. 98—100°.

Methylation of Karaya Gum.—Methylations by methyl sulphate and sodium hydroxide were carried out in an atmosphere of nitrogen at >15°. The dry powdered gum (45 g.) was slowly added with stirring to 30% aqueous sodium hydroxide (500 c.c.) at 0°. More sodium hydroxide (400 c.c.) was added, followed by methyl sulphate (560 c.c. dropwise). The mixture was stirred overnight and then dialysed for 48 hr. The solution was concentrated to small volume, and another methylation was carried out. After four methylations the partly methylated acidic polysaccharide was freed from inorganic material by dialysis. The solution was evaporated to a light brown solid (36·0 g.) (Found: OMe, 33·6; sulphated ash, 8·2%) which was dissolved in water and neutralised with silver carbonate. The silver salt was dried *in vacuo* at 60° (P_2O_5) and was stirred with boiling methyl iodide. After two such methylations with silver oxide and methyl iodide the methylated polysaccharide was obtained as a pale yellow solid (33·5 g.) (Found: OMe, 39·2%). This (20 g.) was separated into four portions when heated under reflux with mixtures (100 c.c. each) of light petroleum (b. p. 38—43°) and chloroform, *viz.*: Fraction I, extracted by light petroleum (90 vols.) and chloroform (10 vols.); a viscous yellow syrup (2·1 g.), $[\alpha]_D^{17}$ +38·3° (*c*, 0·533 in MeOH). Fraction II, extracted by light petroleum (85 vols.) and chloroform (15 vols); a cream-coloured powder (6·4 g.), $[\alpha]_D^{17}$ +41·2° (*c*, 0·335 in MeOH) (Found: OMe, 39·9%). Fraction III, extracted by light petroleum (80 vols.) and chloroform (20 vols.); a pale yellow powder (12·0 g.), $[\alpha]_D^{17}$ +41·2° (*c*, 0·461 in MeOH) (Found: OMe, 40·4%). Fraction IV, extracted by light petroleum (70 vols.) and chloroform (30 vols.); a yellow solid (1·5 g.), $[\alpha]_D^{17}$ +40·3° (*c*, 0·337 in MeOH) (Found: OMe, 38·5%).

The methylated polysaccharide (fraction III; 9·5 g.) was hydrolysed with 90% formic acid at 95° for 28 hr. Formic acid was removed under reduced pressure, last traces being eliminated by repeated dilution with water and evaporation. The residual solution was neutralised with barium carbonate, and the filtrate evaporated to a light brown solid which was extracted with boiling ether. The extracts were evaporated to a syrup (fraction A; 4·0 g.) containing the methylated sugars, which gave on a paper chromatogram sprayed with aniline oxalate a pattern consisting of six spots of R_G 1·01 (yellow-brown), 0·88 (red-brown), and 0·82 (brown), 0·71 (red-brown), 0·55 (yellow-brown), and 0·45 (red-brown) respectively. The residue was dissolved in water and freed from barium ions by sulphuric acid, and the filtrate was evaporated to a syrup (fraction B; 4·1 g.) containing the methylated uronic acids, which gave four spots on a paper chromatogram sprayed with aniline oxalate of R_G 0·82, 0·49, 0·32 (all cerise), and 0·29 (brown) respectively.

Identification of the Neutral Sugars in Fraction A.—The material was separated into eight fractions by partition chromatography on a column of powdered cellulose with as mobile phase 3 : 2 light petroleum (b. p. 100—120°)–*n*-butanol saturated with water. The solvent was removed from each fraction by distillation, the residue in each case taken up in water and treated with charcoal, and the filtrate evaporated to a syrup. The results are tabulated. Fraction AI gave an aniline derivative, m. p. and mixed m. p. 111—112° (Found: OMe, 34·3. Calc. for $C_{15}H_{23}O_4N$: OMe, 33·1%). In fraction AII the relative proportions of trimethyl rhamnose and tetramethyl galactose, from the optical rotation and methoxyl content of the mixture, were 15 and 85% respectively. Fraction AIII gave an aniline derivative, m. p. and mixed m. p. 192° (Found: OMe, 40·8. Calc. for $C_{16}H_{25}O_5N$: OMe, 39·9%). In

fraction AIV the relative proportions of tetramethyl galactose and dimethyl rhamnose, calculated from the optical rotation and methoxyl content of the mixture, were 55 and 45% respectively. Fraction AV was oxidised with bromine water until non-reducing. The solution was worked up in the usual way and the product converted into the amide with liquid ammonia. The product crystallised on being seeded with 3 : 4-dimethyl rhamnonamide, and had m. p. and mixed m. p. 154—156°. Fraction AVI, in 2% methanolic hydrogen chloride kept at room temperature, was observed polarimetrically: $[\alpha]_D$ +40·4° (initial); +23·3° (20 hr.); −3·8° (44 hr.); −22·0° (68 hr.); −40·4° (170 hr.). The syrup was oxidised with bromine water, giving 2 : 3 : 6-trimethyl D-galactonolactone, which crystallised from ether as needles, m. p. and mixed m. p. 98—99° (Found: equiv., 223. Calc. for $C_9H_{16}O_6$: equiv. 220). Fraction AVII (Found for 4-methyl L-rhamnose: R_G 0·59) crystallised spontaneously as rosettes, m. p. 115° (after recrystallisation from ether). A portion (0·101 g.) was boiled with 1% methanolic

Fraction	Yield (%, w/w)	$[\alpha]_D^{18}$ (*c*)	Found: OMe (%)	Sugars present	R_G	Formula	Calc.: OMe (%)
AI	10·5	25·5° (1·1)	44·4	2 : 3 : 4-Trimethyl rhamnose	1·01	$C_9H_{18}O_5$	45·1
AII ...	8·0	103·6° (0·734)	51·3	2 : 3 : 4 : 6-Tetramethyl galactose	1·01 0·88	— —	— —
AIII ...	13·7	103·5° (1·01) [1]	51·3	2 : 3 : 4 : 6-Tetramethyl galactose	0·88	$C_{10}H_{20}O_6$	52·5
AIV ...	20·4	68·9° (1·048)	44·1	3 : 4-Dimethyl rhamnose	0·88 0·84	— —	— —
AV	1·1	19·7° (0·76) [2]	31·9	3 : 4-Dimethyl rhamnose	0·82	$C_8H_{16}O_5$	32·3
AVI ...	16·2	—	41·5	2 : 3 : 6-Trimethyl galactose	0·71	$C_9H_{18}O_6$	41·9
AVII ...	9·5	39·1° (1·13) [3]	18·4	Monomethyl rhamnose	0·55	$C_7H_{14}O_5$	17·4
AVIII...	1·8	—	29·0	2 : 6-Dimethyl galactose	0·45	$C_8H_{16}O_6$	29·8

[1] Changed to 105·6° in 27 days. [2] Changed to 26·8° in 8 days. [3] Changed to 36·6° in 35 days.

hydrogen chloride (30 c.c.), $[\alpha]_D$ +15·0° (initial) changing to −51·1° (const.) in 6 hr. The methylglycoside was isolated by neutralisation of the solution with silver carbonate and evaporation of the filtrate to a syrup (0·106 g.) (Found: OMe, 32·6. Calc. for $C_8H_{16}O_5$: OMe, 32·3%). A portion (18·3 mg.) was dissolved in water (115 c.c.) and treated with 0·31M-sodium metaperiodate (2 c.c.) in the presence of potassium chloride (1 g.). After 8 days' shaking there was no uptake of oxidant. Methylation of a portion of the methylglycoside with Purdie's reagents gave (after hydrolysis to the free sugar) 2 : 3 : 4-trimethyl rhamnose, the identity of which with an authentic specimen was shown chromatographically. A portion of fraction AVII was oxidised with bromine water. The product had $[\alpha]_D$ −27·2° (initial; *c*, 0·8) ⟶ −20·1° (44 hr.) (Found: OMe, 19·6. Calc. for $C_7H_{12}O_5$: OMe, 17·6%) {cf. methyl γ-L-rhamnonolactone, $[\alpha]_D$ −28° (initial) ⟶ −21° (16 hr.) (Hough and Jones, *J.*, 1950, 1202)}. Fraction AVIII had m. p. 106—108° (after recrystallisation from ether), not depressed on admixture with 2 : 6-dimethyl galactose.

Methylated Uronic Acids from Fraction B.—The material was separated into four fractions by partition chromatography on a column of cellulose with 4 : 1 (vol.) butanol–acetic acid saturated with water as mobile phase. The solvent was removed from each fraction and the residues were treated in water with charcoal and the filtrates evaporated to the following pale yellow solid fractions: BI (1·325 g.), probably a dimethyl D-galacturonolactone, R_G 0·82, $[\alpha]_D$ +82·8° (initial; *c*, 0·785) ⟶ +86·4° (11 days) (Found: OMe, 33·9%; equiv., 200). BII, 2 : 4(or 3 : 4)-*dimethyl* D-*galacturonic acid* (0·384 g.), R_G 0·49, $[\alpha]_D$ +91·4° (initial; *c*, 0·52) ⟶ +89·4° (12 days) (Found: OMe, 27·8%; equiv., 215. $C_8H_{14}O_7$ requires OMe, 27·9%; equiv., 222). BIII (0·54 g.), R_G 0·32, $[\alpha]_D$ +94·5° (initial; *c*, 0·785) ⟶ +98·1° (14 days) (Found: OMe, 18·3%; equiv., 224). BIV (0·855 g.), R_G 0·29, $[\alpha]_D$ +66·9° (initial; *c*, 0·595) ⟶ +74·8° (20 days) (Found: OMe, 17·9%; equiv., 176). The OMe contents and equivalent weights of BIII and BIV indicate that they consisted mainly of monomethyl D-galacturonic acid.

A solution of a portion of BII in 1% methanolic hydrogen chloride (kept at room temperature) was observed polarimetrically: $[\alpha]_D$ +69·9° (initial; *c*, 0·8); +55·8° (41 hr.); +55·8° (4 days); +57·4 (13 days). It is improbable, therefore, that this substance contains a free hydroxyl group at $C_{(4)}$. Fractions BI, BIII, and BIV were examined with respect to (*a*) their change in optical rotation in 1% methanolic hydrogen chloride at room temperature, (*b*) the behaviour of the methyl ester of their methylglycosides on periodate oxidation, and (*c*) their conversion into esters of methylated mucic acids, but no certain identifications were achieved.

Periodate Oxidation of Karaya Gum.—(1) *Determination of formic acid produced.* The method of Halsall, Hirst, and Jones (*J.*, 1947, 1399, 1427) was used. The acidic deacetylated polysaccharide (104·2 mg.) was suspended in water (100 c.c.) in a 250-c.c. stoppered bottle, and

sodium metaperiodate solution (0·207M; 10 c.c.) was added. A blank was also prepared. The bottles were shaken continuously in diffuse daylight and at intervals 5-c.c. portions of the clear supernatant liquid were removed and, after the addition of ethylene glycol (1 c.c.), were titrated with 0·01N-barium hydroxide (methyl-red). A suspension of karaya gum in water was neutral to methyl-red. The following results (g. of polysaccharide/mole of $H{\cdot}CO_2H$) were obtained: 19 hr., 368; 43 hr., 260; 66 hr., 213; 115 hr., 186; 139 hr., 171; 163 hr., 164; 191 hr., 152; 257 hr., 136; 615 hr., 104.

(2) *Uptake of periodate.* In the first of the above-mentioned experiments the periodate uptake was estimated at suitable intervals. A 5-c.c. sample was diluted to 20 c.c., and saturated sodium hydrogen carbonate solution (10 c.c.) was added, followed by excess of solid potassium iodide and standard sodium arsenite solution. After 15 min. the excess of arsenite was back-titrated with standard iodine solution. The following results (g. of polysaccharide/mole of $NaIO_4$ uptake) were obtained: 19 hr., 179; 43 hr., 153; 66 hr., 134; 115 hr., 119; 139 hr., 106.

Examination of the Hydrolysis Products from Oxidised Karaya Gum.—The dry purified polysaccharide (0·406 g.) was oxidised with potassium periodate. The oxidation was stopped by the addition of excess of ethylene glycol after 48 hr.; 1 mole of formic acid had been liberated by 270 g. of gum. The mixture, containing the insoluble degraded polysaccharide, was dialysed and evaporated to a white solid (0·21 g.) which was hydrolysed with boiling N-sulphuric acid: $[\alpha]_D$ +17·2° (15 min.); +26·6° (35 min.); +32·4° (95 min.); +38·1° (3 hr., constant). The solution was neutralised with barium carbonate, the filtrate was evaporated to dryness, and the neutral reducing sugars were extracted by boiling methyl alcohol. Evaporation of the solvent gave a syrup (0·070 g.), which was shown to contain rhamnose and galactose in the ratio of 1 : 0·75 (mole) (quantitative chromatographic method).

Another sample of the polysaccharide (0·407 g.) was oxidised for 9 days, 1 mole of formic acid being liberated by 232 g. The oxidised polysaccharide was isolated (0·20 g.) and hydrolysed as before: $[\alpha]_D$ −25·0° (15 min.); +25·0° (2 hr., constant). Determination of the neutral reducing sugars showed the presence of rhamnose and galactose in the ratio of 1 : 0·17 (mole).

We thank the Department of Scientific and Industrial Research for the award of a maintenance allowance to one of us (S. D.) during the early stages of this work, and Dr. J. K. N. Jones for his interest.

THE UNIVERSITIES OF MANCHESTER and EDINBURGH. [*Received, March 30th*, 1953.]

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477. *The Thermochemistry and Pyrolysis of Bishydroxymethyl Peroxide.*

By A. D. JENKINS and D. W. G. STYLE.

The heats of formation of bishydroxymethyl peroxide in the solid and in the gaseous state and in aqueous solution have been determined. The decomposition of the vapour has been investigated at low pressures and at temperatures between 100° and 200°. The products are explicable in terms of two modes of decomposition, one yielding formaldehyde and the hydroperoxide, and the other hydrogen and formic acid. As the temperature was raised, the hydroperoxide became increasingly unstable and could not be isolated above 200°.

ALTHOUGH bishydroxymethyl peroxide is frequently found among the products of the reaction of a number of simple organic molecules with oxygen, very little is known about the properties of its vapour. As normally prepared, this substance contains about 1% of impurities, which appear to be mainly inclusions of solvent and perhaps of polymeric formaldehyde and hydrogen peroxide. The removal of the last traces of these impurities is difficult and hazardous, since the peroxide may explode violently if heated too strongly, and prolonged exposure to vacuum, especially in the presence of phosphoric oxide, can produce a product which approaches nitrogen iodide in sensitivity. A somewhat impure material has consequently been used for the investigation of the thermochemistry and thermal decomposition of the peroxide, and no great precision is claimed for the measurements. The final thermochemical results may be in error by 4 or 5 kcal.

Experimental

Preparation and Estimation of Peroxide.—Bishydroxymethyl peroxide was prepared by vacuum-concentration over concentrated sulphuric acid of a mixture of 35% aqueous formaldehyde (2 mols.) with 30% aqueous hydrogen peroxide (1 mol.). The thick syrup first obtained gradually crystallised. The crystals were filtered off and twice recrystallised from freshly redistilled ether, the ethereal solution being dried (Na_2SO_4). The product was 98—99% pure according to the volume of hydrogen evolved when it was treated with excess of concentrated sodium hydroxide solution, and *ca.* 98% by titration with ceric sulphate. Since ceric sulphate does not react with the peroxide but only with its hydrolysis product, H_2O_2 (Dunicz, Perrin, and Style, *Trans. Faraday Soc.*, **1951**, **47**, 1210), this determination was carried out by adding an excess of standard ceric sulphate solution to a known weight of peroxide, making the solution strongly acid with concentrated sulphuric acid, and heating the solution to 70° for 10 minutes, whereby complete hydrolysis to hydrogen peroxide, which immediately reacted with ceric sulphate, was accomplished. After the solution had cooled to room temperature, the excess of ceric sulphate was back-titrated with standard hydrogen peroxide solution.

Thermochemical Measurements.—Latent heat of sublimation. This was obtained from the temperature dependence of the vapour pressure, which was measured by a dynamic method. B.D.H. " Extra pure " benzene for molecular-weight determinations, which was found to be quite inert toward the peroxide, was used as the carrier gas. The benzene vapour at a constant pressure of 20 mm. Hg was passed slowly through a 100-cm. length of tubing of 5-mm. bore loosely packed with crystalline peroxide, the time of contact being about 10 sec. Following this saturator and in the same thermostat was a length of capillary tubing, across which the gas pressure fell sufficiently to prevent condensation of peroxide vapour in the subsequent tubing exposed to the atmosphere which led to the trap cooled in solid carbon dioxide–alcohol in which all the benzene and peroxide were frozen out. The system was evacuated with a " Hyvac " oil-pump. At the end of an experiment, which lasted 2—6 hours, the trap containing the condensate was removed, stoppered, warmed to room temperature, and weighed. The peroxide content was titrated with ceric sulphate as described above, and after being washed and dried, the empty trap was again weighed. The vapour pressure of the peroxide was calculated from these data, it being assumed that both vapours behaved as perfect gases and were unassociated. Reduction of the rate of flow to about half the usual value did not alter the calculated vapour pressure.

The smallness of the vapour pressure below 15°, and evidence of decomposition of the solid peroxide above 40°, limited the usable temperature range. The results are given below. The values for 15° are rather high, but the others are well represented by $\log p = 15{\cdot}423 - 4910/T$, corresponding to a latent heat of sublimation of 22·5 kcal. mole^{-1} (94·2 kJ mole^{-1}).

T	15·0°	20·1°	25·0°	30·0°	34·8°	39·3°
p, mm.	0·039, 0·034	0·049	0·070	0·167, 0·160	0·302	0·524

Heat of solution. The heat of solution of the peroxide in water was determined calorimetrically. The calorimeter, a Dewar flask of about 500-ml. capacity, was supported in a thermostat kept at 25°. The top of the flask was closed by a cork stopper through tubes inserted into which passed the small electrically-operated stirrer, a Beckmann thermometer used as an indicating instrument, and the leads to the heating coil by means of which the heat capacity of the calorimeter and its contents was calibrated. The heat absorbed when one mole of peroxide was dissolved was independent of the final concentration over the range investigated, as shown by the following data. The average value of the heat of solution, $-\Delta H_s$, at 25° is 5·25 kcal. mole^{-1} (22·0 kJ mole^{-1}).

Final molarity	0·0435	0·0556	0·0943	0·1428	0·1652
$-\Delta H_s$, kcal. mole^{-1}	5·22	5·41	5·21	5·16	5·25

Heat of reaction $[CH_2{\cdot}OH]_2O_2 + 2NaOH \longrightarrow 2H_2 + 2H{\cdot}CO_2Na$. The decomposition of the peroxide is strongly catalysed by hydroxyl ion and in the presence of 2N-sodium hydroxide it is very rapid, as is also the rate of solution of the solid peroxide. The heat evolved ($-\Delta H_1$) when various amounts of solid peroxide were added to 100 ml. of 2N-alkali solution are collected below. The average of the last four is $-\Delta H_1 = 69{\cdot}8$ kcal. mole^{-1} (292·0 kJ mole^{-1}).

Peroxide, m.-moles	0·553	1·085	1·819	2·149	2·298
$-\Delta H_1$, kcal. mole^{-1}	62·5	69·1	69·7	71·6	68·9

The formation of gaseous hydrogen introduces an uncertainty, for were all the hydrogen to remain in solution a correction for this heat of solution, estimated at +0·6 kcal. (from the variation of solubility with temperature, Landolt–Börnstein, " Tabellen," 5th Edn., p. 763), would be necessary, whereas if all the hydrogen escapes saturated with water vapour the corresponding latent heat correction is −0·3 kcal. There was, in fact, a brisk evolution of hydrogen and the correction will be applied on the assumption that none remained in solution :

$$2NaOH(2N) + [CH_2{\cdot}OH]_2O_2\ (cryst.) \longrightarrow 2H_2O\ (liq.) + 2H{\cdot}CO_2Na\ (soln.) + H_2\ (gas) - \Delta H_1 = 70{\cdot}1\ kcal.\ (293{\cdot}2\ kJ)$$

The heat of formation of the crystalline peroxide from its elements ($-\Delta H_f$) may be obtained from ΔH_1 with the aid of Bichowski and Rossini's data (" Thermochemistry of Pure Substances," Reinhold, New York, 1936) for the heat of formation of sodium formate in dilute aqueous solution, $-\Delta H_2 = 157{\cdot}3$ kcal. mole^{-1}, the heat of formation and the differential heat of solution of crystalline sodium hydroxide, $\Delta H_3 = 102{\cdot}0 + 10{\cdot}5 = 112{\cdot}5$ kcal., and the heat of formation and differential heat of solution of liquid water $\Delta H_4 = 68{\cdot}4 + 0 = 68{\cdot}4$ kcal. The heats of formation apply to 291° K. Rough estimates indicate that the use of these in conjunction with ΔH_1 obtained at 298° K. will not introduce any error exceeding the experimental uncertainty. We then have,

$$\Delta H_f,\ [CH_2{\cdot}OH]_2O_2\ (cryst.) = 2\Delta H_2 + 2\Delta H_4 - \Delta H_1 - 2\Delta H_3 = -156{\cdot}3\ kcal.\ mole^{-1}\ (653{\cdot}8\ kJ\ mole^{-1})$$

and from the heat of solution and latent heat of sublimation (all in kcal. mole^{-1})

$$\Delta H_f,\ [CH_2{\cdot}OH]_2O_2\ (gas) = -133{\cdot}8;\quad \Delta H_f,\ [CH_2{\cdot}OH]_2O_2\ (aq.\ soln.) = -151{\cdot}0$$

With the additional heats of formation (Bichowski and Rossini, *op. cit.*)

$$\Delta H_f,\ H{\cdot}CO_2H\ (gas) = -88{\cdot}7;\quad \Delta H_f\ (CH_2O,\ gas) = -28{\cdot}3;\quad \Delta H_f\ (CH_2O,\ aq.) = -43{\cdot}3$$
$$\Delta H_f,\ H{\cdot}CO_2H\ (aq.) = -100{\cdot}2;\quad \Delta H_f\ (H_2O_2,\ gas) = -33{\cdot}6;\quad \Delta H_f\ (H_2O_2,\ aq.) = -45{\cdot}7$$

we obtain

$$[CH_2{\cdot}OH]_2O_2\ (aq.) \longrightarrow H_2\ (gas) + 2H{\cdot}CO_2H\ (aq.);\quad \Delta H = 49{\cdot}4\ kcal.\ (206{\cdot}6\ kJ)$$
$$\longrightarrow 2CH_2O\ (aq.) + H_2O_2\ (aq.);\quad \Delta H = +18{\cdot}7\ kcal.\ (78{\cdot}2\ kJ)$$
$$[CH_2{\cdot}OH]_2O_2\ (gas) \longrightarrow H_2\ (gas) + 2H{\cdot}CO_2H\ (gas);\quad \Delta H = -43{\cdot}6\ kcal.\ (182{\cdot}4\ kJ)$$
$$\longrightarrow 2CH_2O\ (gas) + H_2O_2\ (gas);\quad \Delta H = +43{\cdot}6\ kcal.\ (182{\cdot}4\ kJ)$$

Products of Thermal Decomposition.—This was intended to be preliminary to a more complete investigation which, however, proved to be impracticable. The peroxide vapour was sublimed from a bulb containing a few g. of solid peroxide, kept at 45°, through a heated tap which slightly restricted the flow and reduced back-diffusion of the decomposition products formed in the immediately following cylindrical reaction chamber of diameter 4 cm. and volume *ca.* 200 ml. Leaving the reaction chamber, the products of decomposition passed through a length of narrow-bore tubing and a tap into two traps, the first to remove undecomposed peroxide (only observed below 150°) and the second cooled in liquid air to remove all products other than hydrogen and carbon monoxide, which were collected by a Töpler pump and transferred to the conventional gas-analysis apparatus. The peroxide reservoir and the reaction chamber were heated by manually controlled oil-baths. Preliminary examination of the condensable products showed the presence of formaldehyde (smell), water (restoration of blue colour to dehydrated copper sulphate), acid, and at lower temperatures hydroperoxide (immediate reaction with acid ceric sulphate solution). In the early experiments oxygen was found among the gaseous products. The amount decreased with time and ultimately became zero. It probably arose from hydrogen peroxide impurity in the organic peroxide. The absence of oxygen in the permanent gases from acceptable experiments indicates that the peroxide present in the condensable products is not hydrogen peroxide. This is confirmed by element balances which are best satisfied if the peroxide is $CH_2(OH){\cdot}O{\cdot}OH$ (hydroxymethyl hydroperoxide), which in low concentration is titratable by ceric sulphate (Dunicz, Perrin, and Style, *loc. cit.*).

It was not practicable to attempt quantitative analysis for all these substances in the products collected from any one run. Each of the above condensable products, other than water, was estimated one at a time in separate runs together with the corresponding amount of hydrogen and carbon monoxide. The results of the individual estimations could then be brought to a common basis—a standard amount of hydrogen.

Formaldehyde was estimated colorimetrically with chromotropic acid (Bricker and Johnson, *Ind. Eng. Chem. Anal.*, 1945, **17**, 400). The first trap was cooled with ice–salt and retained the organic peroxides which would otherwise have been hydrolysed to additional formaldehyde during the estimation. Formic acid was estimated by titration with 0·02N-sodium hydroxide

to pH 7. Peroxide was estimated by titration with ceric sulphate in strongly acid solution. The variation with temperature of the molar proportions of the various products scaled to one mole of hydrogen is shown in Fig. 1. At the highest temperature, peroxide formation was negligible and the proportions of the products were those to be expected from

$$[CH_2{\cdot}OH]_2O_2 \longrightarrow H_2 + 2H{\cdot}CO_2H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$[CH_2{\cdot}OH]_2O_2 \longrightarrow H_2O + CH_2O + H{\cdot}CO_2H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

together with a small amount of decomposition of formic acid into water and carbon monoxide.

The appearance of increasing amounts of peroxide as the temperature is reduced required a third decomposition process. The reaction (3) is consistent with the observations at tem-

$$[CH_2{\cdot}OH]_2O_2 \rightleftarrows CH_2O + CH_2(OH){\cdot}O{\cdot}OH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

peratures above 150°. Below this temperature there is obviously a small discrepancy in the analysis, there being either too little formaldehyde or too much hydroperoxide. Since it only occurs when some of the initial peroxide remains undecomposed, the discrepancy probably arises from the partial titration of undecomposed bishydroxymethyl peroxide which would give too large amounts of peroxidic products. An estimated correction, varying from zero at 150° to 10% at 120°, has been applied to the amount of hydroperoxide found before deriving

FIG. 1.

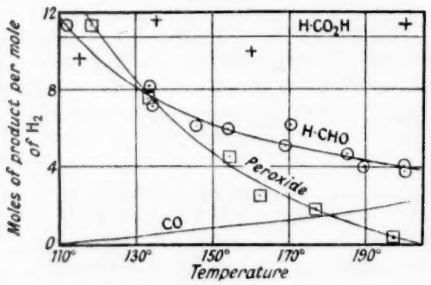
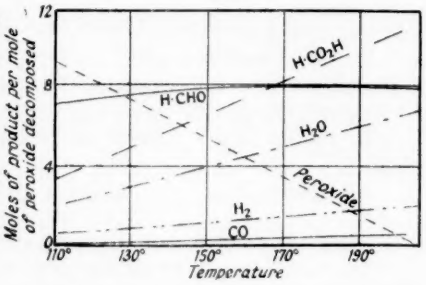


FIG. 2.



the data upon which are based the curves of Fig. 2, which shows how the products from one mole of bishydroxymethyl peroxide vary with the temperature.

Whereas bishydroxymethyl peroxide loses one formaldehyde molecule fairly easily, indeed more readily than it breaks down into hydrogen and formic acid, the loss of the second molecule of formaldehyde by hydroxymethyl hydroperoxide appears to occur to a negligible extent compared with the decomposition into water and formic acid. The heat of formation of gaseous bishydroxymethyl peroxide from gaseous formaldehyde and hydrogen peroxide [$\Delta H = -43{\cdot}6$ kcal. mole^{-1} (182·4 kJ mole^{-1})] is so large that the reverse dissociation would scarcely have been expected. It is regrettable that there is no easy means of obtaining ΔS of this reaction, and hence its equilibrium constant. Evidence for the formation of bishydroxymethyl peroxide in this way is perhaps to be found in the presence of bishydroxymethyl peroxide among the products of the oxidation of gaseous formaldehyde at *ca.* 300° (Bone and Gardner, *Proc. Roy. Soc.*, 1936, *A*, **154**, 297) and of the (heterogeneous?) reaction in a Pyrex vessel at 100° (E. C. A. Horner, unpublished). Reaction (3) is thus probably a reversible reaction, which may well be very largely repressed in the presence of a large excess of formaldehyde such as would be present in most investigations of its oxidation. Since reaction (2) presumably represents the final result of (3), followed by decomposition of the hydroperoxide into water and formic acid, decomposition of bishydroxymethyl peroxide in the presence of excess of formaldehyde should be relatively slow and proceed very largely according to reaction (1), with a ratio of formic acid to hydrogen in the products of 2 : 1, or a little greater if reaction (3) is not completely suppressed. Ratios of this magnitude have been obtained by Summers at 200° and 250° [$(H{\cdot}CO_2H)/(H_2) = 2{\cdot}7$ and $2{\cdot}2$, respectively] (Summers and Style, *Trans. Faraday Soc.*, 1946, **42**, 388) in the photochemical oxidation of formaldehyde. Similar values have also been obtained by E. C. A. Horner from the same reaction.

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KING'S COLLEGE, STRAND, W.C.2. [*Received, November 14th*, 1952.]

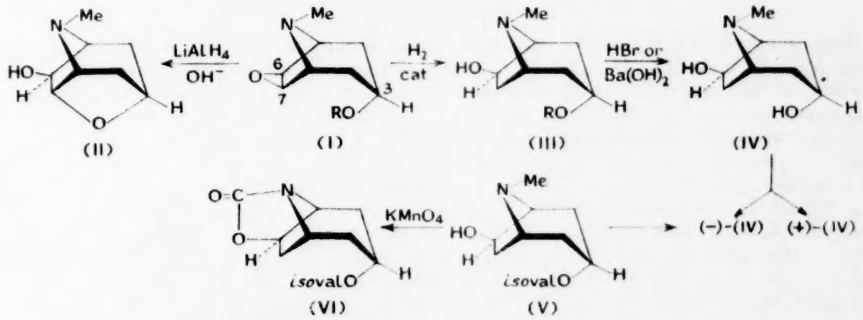
478. *The Stereochemistry of the Tropane Alkaloids. Part III.* The Configuration of Scopolamine and of Valeroidine.*

By GÁBOR FODOR and ÖDÖN KOVÁCS.

Scopolamine was converted by hydrogenolysis into (±)-3 : 6-dihydroxytropane, which was resolved. The (−)-isomer was identical with the alkamine from valeroidine (Fodor, Kovács, and Mészáros, *Research*, **1952**, **5**, 534). Scopolamine and valeroidine are both β-orientated at $C_{(6)}$ since valeroidine forms a cyclic urethane and, as scopoline can be formed from scopolamine only if the $C_{(3)}$-hydroxyl group in the latter is α-orientated with respect to the nitrogen bridge, the configuration at $C_{(3)}$ in valeroidine must be the same as that in scopolamine and tropine.

WHEREAS definite steric structures can be assigned to the epimeric 2-amino-alcohols (cf. Fodor and Kiss, *J.*, 1952, 1589; Fodor and Koczka, *J.*, 1952, 850; Fodor, Kiss, and Bánfi, *Monatsh.*, 1952, **83**, 1146), to tropine and ψ-tropine (Fodor and Nádor, *J.*, 1953, 721), and to the cocaine epimers (Fodor and Kovács, *J.*, 1953, 724), the configurations of those tropane alkaloids that cannot be hydrolysed to tropines or ecgonines are uncertain. Although Willstätter and Berner (*Ber.*, 1923, **56**, 1096) indicated the four projection formulæ possible for scopolamine, no choice between them has hitherto been possible.

In alkaline solution, scopolamine (I; R = CO·CHPh·CH_2·OH) and scopine (I; R = H), but not ψ-scopine, are converted into scopoline (oscine) (II) (Willstätter and Berner, *loc. cit.*), a tetrahydrofuran derivative. It was therefore suggested (Fodor, *Nature*, 1952, **170**, 278) that the rearrangement involved a nucleophilic rearward attack by the $C_{(3)}$-oxygen atom on the $C_{(6:7)}$-epoxide ring; this seems possible if the $C_{(3)}$-hydroxyl is α and the $C_{(6:7)}$-epoxide group is β with respect to the nitrogen bridge,† the nucleophilic character of the hydroxyl group then being enhanced by the alkali present. This suggests that scopolamine and scopine are 6 : 7β-epoxy-3α-hydroxytropanes (as I) (Fodor, *Nature*, *loc. cit.*; cf. Fodor, *Proc. Chem. Acad. Sci. Hungar.*, 1952, **2**, 43).



Evidence on the stereochemistry of the epoxide group appeared to be obtainable by correlation of scopolamine with a derivative of 3 : 6-dihydroxytropane, *e.g.*, valeroidine (V) in which the β-orientation of the $C_{(6)}$-hydroxyl group is already established by the conversion of valeroidine into a cyclic derivative (VI) (Martin and Mitchell, *J.*, 1940, 1155; Mitchell and Trautner, *J.*, 1947, 1330). The details of this correlation are now described (cf. Fodor, Kovács, and Mészáros, *Research*, 1952, **5**, 534).

Attempted hydrogenolysis of scopolamine hydrobromide with lithium aluminium hydride gave only scopoline (II), presumably because of the greater nucleophilic effect of the lithium aluminium scopine complex. However, hydrogenolysis at 150 atm. with a Raney nickel catalyst at 25°, followed by hydrolysis of the ester hydrobromide mixture (III), gave (±)-3 : 6-dihydroxytropane (IV) and (−)-tropic acid. The racemate proved identical with that afforded by the Robinson synthesis (Stoll, Becker, and Jucker, *Helv.*

* Part II, *J.*, 1953, 724. † For details of the nomenclature used see *J.*, 1953, 722.

Chim. Acta, 1952, **35**, 1263). The dibenzoate could not be resolved by use of α-bromo-(+)-camphor-π-sulphonic acid or (+)-tartaric acid, but the racemate itself was resolved in good yield by the use of (lævorotatory) dibenzoyl-(+)-tartaric acid or (+)-tartaric acid; with the former the derivative of (−)-3 : 6-dihydroxytropane separated first, with the latter that of the (+)-isomer was the less soluble. The lævorotatory form was identical with an authentic specimen * of (−)-3 : 6-dihydroxytropane, obtained by hydrolysis of valeroidine (V) (Barger, Martin, and Mitchell, *J.*, 1930, 1820).

The configurational correlations of the epoxide bridge in scopolamine and the $C_{(6)}$-hydroxyl group of valeroidine, and of the corresponding $C_{(3)}$-hydroxyl groups, are thus reasonably established. Since the β-orientation of the $C_{(6)}$-hydroxyl group in (−)-6-hydroxynor-3-tropyl *iso*valerate and in (±)-3 : 6-dihydroxytropane has been proved, the epoxide ring in scopolamine must also be β-orientated with respect to the nitrogen bridge. The $C_{(3)}$-hydroxyl group in (I) can only be α, since the formation of scopoline would otherwise be less feasible. Scopolamine (I) is therefore a 6 : 7β-epoxy-3α-hydroxytropane, as previously suggested, and valeroidine (V) the *iso*valerate of 3α : 6β-dihydroxytropane. Additional evidence on the proximity of the $C_{(6)}$-hydroxyl group and the nitrogen bridge in 3 : 6-dihydroxynortropane is now being obtained by the acyl-migration method.

The ready conversion of scopine into a tetrahydrofuran derivative, involving $C_{(3)}$ and $C_{(6)}$, suggests that the piperidine ring is in the chair form; this is supported by the difficulty of bridging the piperidine ring in *syn*-tropine derivatives. Recent investigations on N ⟶ O acyl migrations in 1-acylpiperidin-4-ols (Fodor and Lestyán, *Magy. Kém. Folyóirat*, in the press) also indicate the greater stability of the chair form in piperidines.

The stereochemistry of teloidine is now being considered.

Added in Proof.—Since this paper was submitted, Meinwald (*J.*, 1953, 712) has independently recorded the same conclusion on the configuration of scopolamine. His deductions are based in part on the formation of scopoline, in part on the structure of scopinium bromide, obtained together with scopolamine *N*-oxide (Polonovski, *Bull. Soc. Chim.*, 1928, **43**, 79). In our opinion, the suggested mechanism of this reaction and the products need further investigation.

Experimental

Hydrogenolysis of Scopolamine.—(a) *With lithium aluminium hydride.* A solution of scopolamine hydrobromide trihydrate (17·52 g., 0·04 mole) and sodium hydrogen carbonate (5·04 g.) in water (90 ml.) was shaken with chloroform (3 × 80 ml.), and the extract dried ($MgSO_4$) and evaporated *in vacuo*, giving a brown oil (12 g.). A solution of this base in dry ether (200 ml.) was added to one of lithium aluminium hydride (3·8 g., 0·1 mole) in ether (300 ml.) during 2·5 hr. at 45°, stirring was continued for 2 hr., and ice-water (8 ml.) was added. After being stirred for a further 2 hr. the ethereal solution was filtered and the residue extracted with ethanol (5 × 100 ml.); this furnished an oil (9·7 g.) on evaporation. An aqueous solution, of pH 3 (hydrochloric acid), was shaken with ether and then evaporated to dryness, giving crystals (6·4 g.); after recrystallisation from ethanol (35 ml.)–ether (45 ml.) (±)-scopoline hydrochloride (5·2 g.) had m. p. 255—257° (Found: C, 50·2; H, 7·1; N, 7·5; Cl, 18·3. Calc. for $C_8H_{13}O_2N,HCl$: C, 50·2; H, 7·2; N, 7·2; Cl, 18·3%). The picrate, m. p. 236—237°, did not depress the m. p. of a specimen from authentic (±)-scopoline (oscine).

(b) *Catalytic hydrogenation.* (i) Commercial scopolamine hydrobromide trihydrate (87·69 g., 0·2 mole) in water (300 ml.) was hydrogenated in the presence of Raney nickel [60 g.; in water (300 ml.)] for 16 hr. at 25° at atmospheric pressure; 6360 ml. (1·4 mol.) of hydrogen were absorbed. The ester hydrobromides were hydrolysed directly in solution or after removal of the solvent.

(ii) Hydrogenation over Raney nickel at 150 atm. pressure consumed the same amount of hydrogen, and gave the same product.

Acetylscopoline. Scopoline (oscine) [obtained by shaking the hydrochloride (3·9 g.) with silver oxide (5 g.) and water (60 ml.) for 30 min.] was boiled with acetic anhydride (7 ml.) for 3 hr. The acetyl derivative formed crystals (1·8 g.), m. p. 56—57°, from light petroleum (Found: C, 60·7; H, 7·6; N, 7·4; Ac, 21·1. Calc. for $C_{10}H_{15}O_3N$: C, 60·8; H, 7·6; N, 7·1; Ac, 21·4%).

The crude derivative was converted into the bromide, which had m. p. 219—220° (from

* The authors are indebted to Dr. M. Mitchell for this sample.

chloroform–light petroleum) (cf. Hess and Wahl, *Ber.*, 1922, **55**, 1979). Neither derivative depressed the m. p. of the corresponding authentic material.

Hydrolysis of the Ester Mixture obtained by Catalytic Hydrogenation.—(a) *With 10% hydrobromic acid.* Water and 46% hydrobromic acid were added to the solution obtained above to give a final volume of 1700 ml., containing 170 g. of hydrobromic acid. The solution was refluxed for 16 hr., then cooled, and extracted with ether. The extracts gave (−)-tropic acid (31·8 g., 95%), m. p. 126—127° (from water), $[\alpha]_D^{25}$ −74° (*c*, 2 in H_2O) (cf. King, *J.*, 1919, **115**, 476). The residue (46·8 g.), obtained from the aqueous solution, gave (±)-3 : 6-*dihydroxytropane hydrobromide* (24·89 g., 52%), m. p. 267° (decomp.) (from ethanol–ether) (Found : C, 40·6; H, 6·6; N, 5·8; Br, 33·85. $C_8H_{15}O_2N$,HBr requires C, 40·3; H, 6·8; N, 5·9; Br, 33·6%).

The free base, obtained by treating the hydrobromide (3·57 g.) in ethanol (30 ml.) with N-sodium hydroxide (15 ml.) and Soxhlet-extracting the product, formed crystals, m. p. 179—180° [from ethanol–ether (1 : 5)] (Found : C, 60·95; H, 9·7; N, 8·9. Calc. for $C_8H_{15}O_2N$: C, 61·1; H, 9·6; N, 8·9%). Stoll *et al.* (*loc. cit.*) record the same m. p. The picrate had m. p. 248—249° (cf. Stoll *et al.*).

(b) *With 10% hydrochloric acid.* The product of the hydrogenation of (−)-scopolamine hydrobromide hydrate (21·9 g.) was treated in water (80 ml.) with sodium carbonate (2·65 g.) and sodium hydrogen carbonate (5·3 g.), and the base isolated, by extraction with chloroform (10 × 20 ml.), and dried. The oil was refluxed for 16 hr. with 10% hydrochloric acid (800 ml.), tropic acid and (±)-3 : 6-dihydroxytropane hydrochloride (4·75 g., 49%), m. p. 295° (decomp.), being obtained.

(c) *With baryta.* The solution obtained from the hydrogenation of scopolamine hydrobromide hydrate (87·69 g.) was diluted with water to 1900 ml. and barium hydroxide octahydrate (110 g.) was added. After 2 hr.' refluxing, barium ions were removed by 50% sulphuric acid, and the aqueous solution extracted with ether. (±)-Tropic acid (30·2 g., 90%), $\alpha = 0°$, m. p. 98—104° (cf. Ladenburg, *Annalen*, 1881, **206**, 302), was obtained from the ether extracts. Trituration with acetone of the residue from the aqueous solution gave (±)-3 : 6-dihydroxytropane hydrobromide (33·8 g., 71%), m. p. 256° (decomp.), from which the (±)-base (20·4 g.), m. p. 177—179°, was obtained.

Barger, Martin, and Mitchell (*loc. cit.*) recorded a similar observation in the hydrolysis of tigloidine.

(±)-3 : 6-*Dibenzoyloxytropane Hydrochloride.*—The (±)-dihydroxy-compound (4·7 g.) was benzoylated with benzoyl chloride (24 g.) at 160° for 2 hr. The *derivative* formed yellow crystals (10·3 g.), m. p. 268° (Found : C, 65·5; H, 5·95; N, 3·25; Cl, 8·8. $C_{22}H_{23}O_4N$,HCl requires C, 65·7; H, 6·0; N, 3·5; Cl, 8·8%).

Attempted Resolution of (±)-3 : 6-*Dibenzoyloxytropane Hydrochloride.*—(a) *With α-bromo-(+)-camphor-π-sulphonic acid.* An aqueous solution (40 ml.) of ammonium α-bromo-(+)-camphor-π-sulphonate (6·57 g.) was added to a suspension of the hydrochloride (8·03 g.) in warm water (60 ml.). The water was removed and the residue extracted with hot ethanol (80 ml.). Long white needles (8·2 g.) separated on cooling; after recrystallisation from ethanol the salt (4·4 g.) had m. p. 218—220°, $[\alpha]_D^{27}$ +59·85 (*c*, 2 in EtOH). A solution of the salt (2·0 g.) in water (20 ml.) was treated with sodium hydrogen carbonate (0·75 g.) and then extracted with chloroform (5 × 20 ml.). Removal of the solvent gave an oil, an alcoholic solution of which was treated with 9·8N-alcoholic hydrochloric acid. The hydrochloride (1·1234 g.) had m. p. 264° (decomp.), $\alpha = 0°$.

(b) *With (+)-tartaric acid.* An aqueous solution (200 ml.) of (±)-3 : 6-dibenzoyloxytropane [from the hydrochloride (8·03 g.)] and (+)-tartaric acid (2·95 g.) was heated to boiling; on cooling, white crystals (6·2 g.), m. p. 130—135°, separated. Repeated recrystallisation gave a salt, m. p. 155—157°, $[\alpha]_D^{27}$ +8·53° (*c*, 2·051 in 50% EtOH).

The free base, obtained from the salt (3·2 g.) and sodium hydrogen carbonate (2·6 g.) in water (40 ml.), was converted into the hydrochloride (2·32 g.), m. p. 265° (decomp.), which was optically inactive.

Resolution of (±)-3 : 6-*Dihydroxytropane with* (+)-*Tartaric Acid.*—*The* (+)-*isomer.* The (±)-base (4·71 g.) and (+)-tartaric acid (4·5 g.) were dissolved in water (60 ml.), which was then removed *in vacuo*. A solution of the residue (9·05 g.) in 78% alcohol (20·5 ml.) was set aside at 1° for 48 hr., giving rhombic crystals (*A*) (2·55 g.) (from 96% alcohol) of the (+)-3 : 6-dihydroxytropane (+)-tartrate hydrate, m. p. 150—151°, $[\alpha]_D^{27}$ +14·23° (*c*, 2·249 in H_2O) (the loss in weight at 120°/30 mm. corresponded to 1 mol. of water of crystallisation).

The anhydrous salt (1·42 g.) was converted, in water, into the picrate (1·54 g.), which was

recrystallised from water, giving the (+)-salt, m. p. 251—252° [mixed m. p. with the (±)-salt 245—246°; Wolfes and Hromatka, *Ber.*, 1934, **47**, 45, record m. p. 153° (decomp.) for the (−)-picrate].

The (+)-picrate (1·22 g.) was converted into the (+)-sulphate by means of 0·2N-sulphuric acid (65 ml.), and the sulphate solution, after removal of picric acid by extraction with ether, shaken for 1 hr. with barium carbonate (2·6 g.). Removal of barium sulphate and evaporation of the solvent *in vacuo* gave the (+)-base (0·4156 g.). After recrystallisation from ethanol (6 ml.)–ether (30 ml.), this had m. p. 209—210°, $[\alpha]_D^{27}$ +24·14° (*c*, 1·988 in EtOH). Barger *et al.* (*loc. cit.*) record m. p. 212° (corr.), $[\alpha]_D$ −25°, for the (−)-form obtained from valeroidine.

The (−)-isomer. The mother liquors, left after removal of the crystal (*A*), were concentrated and the amorphous residue (5·7 g.) converted in water into the picrate, a mixture, m. p. 246—248° (from water), of the (±)- and the (−)-form being obtained. A suspension in 0·2N-sulphuric acid was extracted several times with ether (1400 ml. in all), sulphate ions were removed by barium carbonate (12 g.), and the solvent was evaporated. After four recrystallisations of the residue from alcohol–ether (5 : 1), the (−)-base, m. p. 209°, $[\alpha]_D^{27}$ −23·31° (*c*, 2·038 in EtOH), was obtained. The m. p. of this was not depressed by an authentic specimen of (−)-**3** : 6-dihydroxytropane, but an admixture with the (+)-form melted at 180°.

Resolution of (±)-**3** : **6**-*Dihydroxytropane with* (*Lævorotatory*) OO′-*Dibenzoyl*-(+)-*tartaric Acid.*—Removal *in vacuo* of the solvent from a solution of the (±)-base (4·71 g.) and *OO′*-dibenzoyl-(+)-tartaric acid (10·74 g.) in 96% alcohol (100 ml.), and slow crystallisation of the hygroscopic solid from 96% alcohol (30 ml.) gave crystals (6·25 g.), m. p. 169—170°, $[\alpha]_D^{20}$ −78° (*c*, 2·0 in 96% EtOH). Further recrystallisation gave (−)-**3** : 6-dihydroxytropane dibenzoyl-(+)-tartrate (2·9 g.), m. p. 172°, of unchanged $[\alpha]_D$.

A suspension of the finely ground salt in N-sulphuric acid (15 ml.) was repeatedly extracted with ether (300 ml. in all), N-sodium hydroxide was then added, and the solution was evaporated. Extraction of the residue with ethanol–acetone (1 : 1) and repeated recrystallisation of the extracted material from ethanol (6 ml.)–acetone (15 ml.) gave the pure (−)-base (0·34 g.), m. p. 210°, $[\alpha]_D^{20}$ −24·33° (*c*, 2·014 in EtOH). This did not depress the m. p. of an authentic specimen, kindly provided by Dr. Mitchell.

The (+)-base was similarly prepared from the first mother-liquor of the preparation of the (−)-base dibenzoyl-(+)-tartrate. The pure isomer (0·54 g.) [from ethanol–acetone (1 : 1)] had m. p. 211°, $[\alpha]_D^{20}$ +24° (*c*, 2·0 in EtOH), and depressed the m. p. of Mitchell's specimen to 180°.

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479. *The Alkaloids of* Gelsemium sempervirens. *Part II.**

By GURNOS JONES and T. S. STEVENS.

Experiments on the Hofmann, Emde, cyanogen bromide, and other processes for the degradation of gelsemine give no support to the formulation of the alkaloid as an allylamine derivative. The presence of an oxindole system having a free imino-group is confirmed, the second (basic) nitrogen atom being methylated. A new process for the degradation of allylamine derivatives by *N*-bromosuccinimide is described.

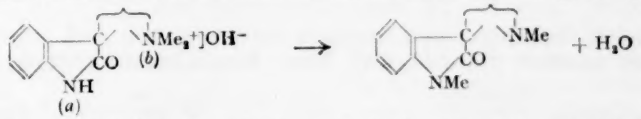
THE recent work of Marion (*J. Amer. Chem. Soc.*, 1950, **72**, 2308; *Helv. Chim. Acta*, 1952, **35**, 638), Prelog (*ibid.*, 1951, **34**, 1139, 1962; 1952, **35**, 640), Witkop (*J. Amer. Chem. Soc.*, 1948, **70**, 1424), and their associates shows that one nitrogen atom—N(*a*)—of gelsemine is involved in a 3 : 3-disubstituted oxindole system, and throws light on the structure of the remainder of the molecule containing the basic N(*b*). We now record observations which in part cover similar ground.

While it was shown (Part I) that gelsemine gave no homogeneous product with cyanogen bromide, dihydrogelsemine yields a cyanamide which can be hydrolysed to a demethyldihydrogelsemine giving on remethylation a material not distinguishable from

* Part I, *J.*, 1945, 579.

dihydrogelsemine methiodide. Since the cyanamide is non-basic, the alicyclic N(*b*) must have been attacked, and this atom therefore carries the methyl group of the alkaloid. The properties of the benzoyl derivative of the demethylated base discouraged any attempt to degrade it further by treatment with phosphorus pentachloride.

Pyrolysis of dihydrogelsemine methohydroxide at 190° gave dihydro-*N*(*a*)-methylgelsemine, prepared meantime under more drastic conditions by Prelog *et al.* (*loc. cit.*):



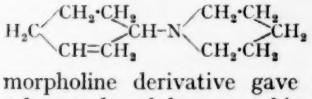
Like these authors we failed to degrade the methohydroxide of the new base. Gelsemine methohydroxide at 190° reverted to the parent alkaloid, in contrast to the transmethylation which they effected at 230—240°.

The proposal (*idem, loc. cit.*) for gelsemine of formulæ containing an allylamine system suggested the application of Emde's method. Since attempted Emde degradation of dihydrogelsemine appeared to give an organo-mercury compound (Part I), we explored the use of mercury-free reagents. Model experiments with sodium–lead alloy (compare Fichter and Stenzl, *Helv. Chim. Acta*, 1933, **16**, 571) gave favourable results with benzyltrimethylammonium iodide in alkaline solution, but with gelsemine methosulphate gave no characterisable product. Emde and Kull (*Arch. Pharm.*, 1936, **274**, 173) found that some quaternary ammonium compounds resistant to sodium amalgam could be degraded by catalytic hydrogenation. Benzyltrimethylammonium iodide was not effectively reduced by hydrogen over platinised charcoal, but the methyl sulphate in acetic acid gave moderate yields of toluene and trimethylamine; gelsemine methosulphate, however, gave no non-quaternary product. With sodium in liquid ammonia, used by Clayson (*J.*, 1949, 2016) to degrade hydrocotarnine methiodide, gelsemine methiodide gave only slightly impure gelsemine. This reagent, which Manske (*J. Amer. Chem. Soc.*, 1950, **72**, 58) found effective in the fission of resistant ethers, was also applied to dihydrogelsemine, since the second oxygen of gelsemine is believed to be ethereal; the base was unaffected.

The action of *N*-bromosuccinimide on tertiary allylamines might be expected to take the course:

$$R{\cdot}CH{:}CH{\cdot}CH_2{\cdot}NR'_2 \longrightarrow R{\cdot}CH{:}CH{\cdot}CHBr{\cdot}NR'_2 \xrightarrow{H_2O} R{\cdot}CH{:}CH{\cdot}CHO + HBr + NHR'_2$$

Cinnamyldimethylamine thus afforded 34% of cinnamaldehyde, and 3 : 3-diphenylallyldimethylamine, $CPh_2{:}CH{\cdot}CH_2{\cdot}NMe_2$, gave 60% of diphenylacraldehyde. Attack at either carbon atom adjacent to the ethylenic system is possible with 3-piperidino- and 3-morpholino-*cyclo*hexene. The reaction with bromosuccinimide did not go smoothly in either case, and no *cyclo*hexenone could be identified. The morpholine derivative gave some 1 : 2-dibromo-3-morpholino*cyclo*hexane, and a little *p*-bromophenol by a combination of bromination, dehydrobromination, and hydrolysis. Gelsemine with bromosuccinimide yielded a water-soluble and an insoluble product; with alkali the former gave a base which quickly changed into an insoluble material apparently identical with that obtained directly. This contained ionisable bromine and from its ultra-violet absorption and other properties appeared to be the bromo-*allo*gelsemine hydrobromide which Prelog *et al.* (*loc. cit.*) obtained by bromination of gelsemine. Braude and Wright (*J.*, 1952, 1120) observe that in presence of tertiary amines, and especially of ammonium salts, bromosuccinimide tends to attack the double bond rather than the "allyl position" of olefins; it is significant that a higher yield of bromo*allo*gelsemine was obtained from gelsemine hydrochloride than from the free base.


(I)

We have thus failed to produce evidence for the existence of an allylamine system in gelsemine. The fact that dihydrogelsemine is a stronger base than gelsemine, by a factor of about 2 in K_b, shows that the alkaloid is not a vinylamine derivative, since cyclic vinylamines are stronger than the corresponding saturated bases (Adams and Mahan, *J. Amer. Chem. Soc.*, 1942, **64**, 2589). Data are lacking as to the relative strengths of allylamines

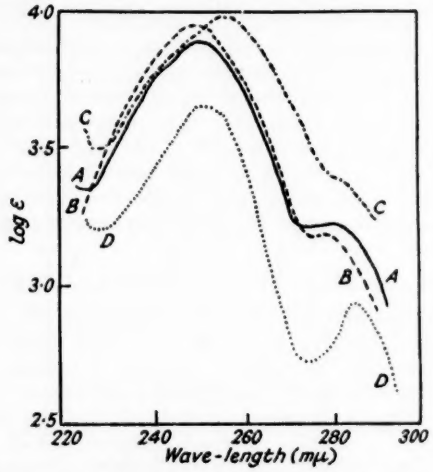
and bases in which the nitrogen atom is more remote from the double bond, but values for phenylated amines (*e.g.*, benzyldimethylamine, K_b $1{\cdot}05 \times 10^{-5}$, compared with trimethylamine, $5{\cdot}27 \times 10^{-5}$) suggest that in gelsemine more than one carbon atom separates the nitrogen atom from the ethylenic system. It is further significant that dihydrogelsemine and its *N*(*a*)-methyl derivative do not undergo Hofmann degradation, for the reduction product of an allylamine must contain at least one hydrogen atom in the β-position to nitrogen.

Several indole derivatives were prepared for comparison with gelsemine and its transformation products. Heated with lime, hexahydrobenzophenylhydrazide gives

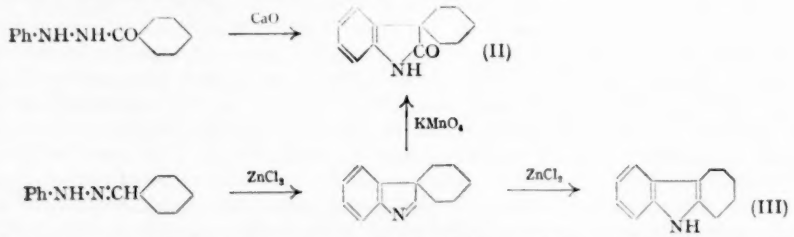
Substance	$\lambda_{max.}$, mμ	$\text{Log}_{10}\ \varepsilon$
2 : 3-Dimethylindole	* 280	3·85
1 : 2 : 3-Trimethylindole	245, 295	4·15, 3·45
*cyclo*Heptenoindole (III)	234, 284	4·05, 3·90
3 : 3-Dimethyloxindole	248, 279 †	3·97, 3·17
*cyclo*Hexane*spiro*oxindole	249, 279	3·94, 3·17 (*B* in Fig.)
Gelsemine	252, 282	3·89, 3·18 (*A* in Fig.)
Dihydrogelsemine	250, 281	3·90, 3·15
Dihydro-*N*(*a*)-methylgelsemine	258, 281 †	3·98, 3·33 (*C* in Fig.)
Cyanodemethyldihydrogelsemine	252, 287	3·65, 2·90 (*D* in Fig.)
Bromo*allo*gelsemine hydrobromide	259	3·87
3 : 3-Dimethylindolenine ‡	255	3·6
*cyclo*Hexane*spiro*indolenine	252	2·6

* Not measured below 245 mμ. † Inflection.

‡ Grammaticakis, *Compt. rend.*, 1940, **210**, 569.



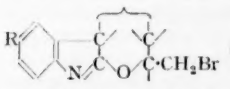
*cyclo*hexane*spiro*-3-oxindole (II), which was also obtained by permanganate oxidation of *cyclo*hexane*spiro*indolenine, the product of a cautious Fischer indole synthesis with hexahydrobenzaldehyde phenylhydrazone :



In the last process, more vigorous treatment led by Wagner–Meerwein ring-enlargement to the isomeric *cyclo*heptenoindole (III; Perkin and Plant, *J.*, 1928, 2583); Brunner

(*Monatsh.*, 1895, **16**, 849) obtained 2 : 3-dimethylindole by heating the zinc chloride complex of 3 : 3-dimethylindolenine. Data on ultra-violet absorption are summarised in the Table; the curves are similar for oxindoles and for gelsemine and all its derivatives, except bromo*allo*gelsemine which absorbs in the same region as 3 : 3-disubstituted indolenines.

Prelog *et al.* (*loc. cit.*) formulate bromo*allo*gelsemine as a cyclic 2-alkoxyindolenine with the partial formula (IV; R = H). With diazobenzenesulphonic acid it gives a yellow dye which becomes deep red in alkali, and on this formulation the normal product of coupling (IV; R = $HSO_3 \cdot C_6H_4 \cdot N{:}N \cdot$) would lack a mobile proton such as would account for the behaviour with alkali. *cyclo*Hexane*spiro*indolenine, on the other hand, does not couple.


(IV)

Hydrogenation of 3 : 3-dimethyloxindole was studied for comparison with that of the alkaloid. Over Adams's catalyst it gave a hexahydro-derivative transparent down to 230 mμ, analogous to the octahydrogelsemine similarly prepared from gelsemine or dihydrogelsemine (*idem, loc. cit.*). A sharply melting, crystalline product isolated after absorption of 2 mols. of hydrogen was a mixture or complex of the hexahydro-compound and dimethyloxindole. Attempts to open the lactam ring of dimethylhexahydro-oxindole failed : hydrochloric acid at 160° had no effect, and baryta gave a product which could not be purified.

Experimental

Gelsemine was isolated from *Gelsemium sempervirens* root, and from the pharmacological extract which yielded little of the thermally unstable sempervirine and no gelsemicine. *Gelsemine methosulphate*, which separated after 10 minutes' boiling of the components in acetone and crystallised from ethanol, had m. p. 298° (decomp.) (Found : N, 5·7; S, 6·3. $C_{22}H_{28}O_6N_2S,C_2H_6O$ requires N, 5·7; S, 6·5%). Hydrogenation of gelsemine over Raney nickel at 150°/100 atm. gave only the known dihydrogelsemine, m. p. 224°. The colour reactions of gelsemine and some indole derivatives were compared :

Substance	Vanillin–HCl	Ehrlich's reagent	H_2SO_4–$K_2Cr_2O_7$
Gelsemine	Pale yellow	Pale green	Red → violet → green
2 : 3-Dimethylindole ...	Yellow → orange	Deep rose → red-violet	—
1 : 2 : 3-Trimethylindole	Yellow → orange	Magenta → red-violet	—
3 : 3-Dimethyloxindole ...	Pale yellow	Pale green	Intense red

Values of pK_b for gelsemine (4·71) and dihydrogelsemine (4·41) were obtained by determining the pH of solutions of the hydrochlorides with a Cambridge pH meter.

Cyanogen Bromide and Dihydrogelsemine.—Mixed dry ethereal solutions of the base (400 mg.) and cyanogen bromide (200 mg.) were boiled for a short time. After some hours the separated solid was crystallised from ethanol, giving N-*cyanodemethyldihydrogelsemine* (320 mg.), m. p. 269° (Found : C, 71·4; H, 6·1. $C_{20}H_{21}O_2N_3$ requires C, 71·6; H, 6·3%). It neither dissolved in dilute mineral acids nor reacted with methyl iodide. Hydrolysis required vigorous conditions : the cyanamide (240 mg.) in concentrated hydrochloric acid (10 c.c.) was heated for 8 hr. at 160°. Basification of the deep red solution with ammonia and extraction with ether gave a white solid which became ether-insoluble on exposure to air (? carbonate formation), and with ethereal picric acid gave *demethyldihydrogelsemine picrate*, prisms (from ethanol), m. p. 281—282° (decomp.) (Found : C, 56·3; H, 4·1. $C_{25}H_{25}O_9N_5$ requires C, 55·7; H, 4·6%). With methyl iodide in acetone, demethyldihydrogelsemine gave needles which, crystallised from ethanol, melted at 300—302° (decomp.), alone or mixed with dihydrogelsemine methiodide. *X*-Ray powder photographs of the two materials (for which we are indebted to Dr. P. Woodward of this Department) seemed identical but could not be distinguished with certainty from that of gelsemine methiodide. Schotten–Baumann benzoylation of demethyldihydrogelsemine gave an uncrystallisable product.

Attempted Hofmann Degradation.—Dihydrogelsemine methiodide (300 mg.) in aqueous solution was shaken with freshly precipitated silver oxide (300 mg.), and the solution boiled, filtered, and evaporated to dryness. The residue, heated for 30 min. at 190°/0·1 mm., gave a colourless sublimate; extraction of the whole with ether, passage through a column of unactivated alumina, and evaporation gave a colourless solid, crystallising from ligroin in prisms, m. p. 163—165°. The methiodide, prepared in acetone and crystallised from ethanol,

had m. p. 289°. Prelog *et al.* (*loc. cit.*) give m. p.s (corr.) 165—166° and 299° for dihydro-*N*(*a*)-methylgelsemine and its methiodide. Prepared in ethanol, the *picrate* had m. p. 216—218° (Found: C, 57·0; H, 5·0; N, 12·4. $C_{27}H_{29}O_9N_5$ requires C, 57·1; H, 5·2; N, 12·3%). The base was unaffected by attempted reduction over Adams's platinum oxide catalyst, and oxidation with potassium permanganate in acetone gave no definable product.

Reductions with Sodium–Lead Alloy.—Benzyltrimethylammonium methyl sulphate (from benzyldimethylamine and methyl sulphate in ether; hygroscopic; 0·7 g.) in water (30 c.c.) was stirred at 3° in a slow current of hydrogen in a flask fitted with a dropping funnel, means of adding sodium–lead alloy, a condenser, and an absorption tube charged with standard acid. The alloy (Goldach, *Helv. Chim. Acta*, **1931**, **14**, 1436) (8 g.), and sulphuric acid when used, were added gradually, the mixture was made alkaline and distilled, and the trimethylamine determined by back-titration of the receiver contents:

Solvent	H_2O 30 c.c.	H_2O 30 c.c.	EtOH 30 c.c.	Na, 1 g., in EtOH, 30 c.c.
Acid added	10N 20 c.c.	2N 50 c.c.	—	—
Yield, %	25	28·5	41·2	59

Hydrohydrastinine methosulphate, prepared in acetone and crystallised from ethanol, had m. p. 188° (Found: S, 10·0. $C_{13}H_{19}O_6NS$ requires S, 10·1%). Reduced as above in alcohol with a little water, it yielded a brown oil giving NN-*dimethyl*-4 : 5-*methylenedioxy*-2-*vinylbenzylamine picrate*, m. p. 181° (Found: C, 50·2; H, 4·0. $C_{18}H_{18}O_9N_4$ requires C, 49·9; H, 4·2%); the same unsaturated base is produced by heating the methosulphate with dilute aqueous sodium hydroxide as the normal product of Hofmann degradation. When the reaction mixture was acidified before evaporation, no non-quaternary base was obtained. Gelsemine methosulphate was treated in the same way, in ethanol.

Other Reductions of Quaternary Salts.—Benzyltrimethylammonium methyl sulphate (346 mg.) absorbed 77·3 c.c. of hydrogen at 23°/758 mm. in acetic acid over platinised charcoal, affording toluene (34%), and trimethylamine (36%; distilled into hydrochloric acid and weighed as hydrochloride). Reduction of 35% of the cation to toluene and trimethylammonium, and the remainder to hexahydrobenzyltrimethylammonium requires absorption of 74·1 c.c. Little hydrogen was absorbed in a parallel experiment on benzyltrimethylammonium iodide in water.

Cinnamyldimethylamine and N-*Bromosuccinimide.*—Cinnamyl bromide (10 g.) and dimethylamine (6 g.) in nitromethane were mixed at −10°, and after 1 hr. the solvent was removed in a vacuum. The basic product of the reaction distilled at 107°/12 mm. (3·9 g.) and the derived cinnamyldimethylamine picrate had m. p. 123—124° (cf. King and Holmes, *J.*, 1947, 164). An oil (2 g.) was also formed, soluble in chloroform but not in ether, and presumed to be impure dicinnamyldimethylammonium bromide. This, heated with concentrated potassium hydroxide solution at 200°, gave equal weights of cinnamyldimethylamine and dicinnamylmethylamine, b. p. 180—182°/0·5 mm. The latter base, for which Blicke and Zienty (*J. Amer. Chem. Soc.*, 1939, **61**, 774) record b. p. 180—185°/5 mm., yielded with methyl iodide in acetone feathery plates of *dicinnamyldimethylammonium iodide*, m. p. 170—170·5° (Found: C, 58·8; H, 6·1. $C_{20}H_{24}NI$ requires C, 59·3; H, 6·0%). To cinnamyldimethylamine (2·19 g.) in dry carbon tetrachloride, *N*-bromosuccinimide (4·38 g.) was added and the mixture boiled for 30 min. When cool, the liquid was filtered from the red gum, shaken with hydrochloric acid which removed cinnamyldimethylamine (0·33 g.), and evaporated, giving more gum which was united with the other and steam-distilled. The distillate afforded cinnamaldehyde (0·52 g.) (oxime, m. p. and mixed m. p. 140°; 2 : 4-dinitrophenylhydrazone, m. p. 242°).

3 : 3-*Diphenylallyldimethylamine and* N-*Bromosuccinimide.*—3 : 3-Diphenylallyl bromide (Masson, *Compt. rend.*, 1902, **135**, 533; Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80) (6 g.) gave, with dimethylamine in nitromethane as above, diphenylallyldimethylamine, b. p. 124°/0·3 mm. (2 g.); Adamson (*J.*, 1949, S 144) gives b. p. 192—193°/18 mm. Treated as before with *N*-bromosuccinimide (0·8 g.), it (0·9 g.) gave unchanged material (40 mg.) and a gum which was boiled with water for 10 min., whereafter extraction with ether gave diphenylacraldehyde (0·47 g.). The semicarbazone melted at 219—221° (Found: N, 15·5. Calc. for $C_{16}H_{15}ON_3$: N, 15·8%); Wittig and Kethur (*Ber.*, 1936, **69**, 2085) give m. p. 217—219°. The 2 : 4-dinitrophenylhydrazone had m. p. 193·5°; Lorenz and Wizinger (*Helv. Chim. Acta*, 1945, **28**, 600) give m. p. 195—196°.

3-*Piperidinocyclohexene and* N-*Bromosuccinimide.*—Piperidinocyclohexene picrate had m. p. 108·5° (Found: C, 51·8; H, 5·8. Calc. for $C_{17}H_{22}O_7N_4$: C, 51·8; H, 5·6%); Bamford and

Stevens (*J.*, 1952, 4735) give m. p. 109—111°. The free base, b. p. 106—108°/15 mm. (3·3 g.), in dry carbon tetrachloride was treated with bromosuccinimide (3·5 g.). The very vigorous reaction produced a red gum which was distilled in steam, but no *cyclo*hexenone could be recognised; the only substance identified was a little unchanged base.

3-*Morpholino*cyclo*hexene and* N-*Bromosuccinimide*.—1 : 2-Dibromo*cyclo*hexane (23 g.) and morpholine (27 g.) were heated at 100° for 2 hr. The mixture was shaken with water and ligroin, and the upper layer washed thoroughly with water, dried, and distilled; 3-morpholino-*cyclo*hexene (13·3 g.) boiled at 110—115°/16 mm.; the *picrate*, needles from ethanol, had m. p. 148—149° (Found: C, 48·9; H, 5·1. $C_{16}H_{20}O_8N_4$ requires C, 48·5; H, 5·1%). A solution of the base (3·34 g.) in carbon tetrachloride became warm on addition of bromosuccinimide (3·56 g.) and deposited a red gum. The filtrate afforded only unchanged base (1·5 g.). Distilled in steam, the gum gave *p*-bromophenol (50 mg.) (benzoyl derivative, m. p. 103—104°); basification of the residual aqueous solution yielded an oil which with ethanolic picric acid gave yellow, halogen-containing needles, m. p. 174—175°, of 1 : 2-*dibromo*-3-*morpholino*cyclo*hexane picrate* (Found: C, 34·9; H, 3·7. $C_{16}H_{20}O_8N_4Br_2$ requires C, 34·5; H, 3·6%).

Gelsemine and N-*Bromosuccinimide*.—Acetone-free gelsemine (250 mg.) was boiled in carbon tetrachloride with bromosuccinimide (275 mg.) for several hours, giving a cream-coloured precipitate which was filtered off after cooling; nothing was obtained from the filtrate. Part of the solid dissolved in boiling water; the solution on basification gave a flocculent precipitate soluble in ether and acetone, which could not be crystallised and passed on evaporation into a product insoluble in ether, apparently identical with the original water-insoluble fraction. This was purified by repeated precipitation from chloroform by ether, giving a very pale yellow powder which decomposed at 310° and had ultra-violet absorption similar to that of bromo-*allo*gelsemine (Found: N, 5·5. Calc. for $C_{20}H_{22}O_2N_2Br_2$: N, 5·8%). With diazobenzene-*p*-sulphonic acid it produced a yellow precipitate giving a deep orange colour with alkali.

3 : 3-*Dimethyloxindole*.—Prepared by Brunner's method (*Monatsh.*, 1897, **18**, 98), crystallised from ethyl acetate, and sublimed (12 mm.), this melted at 154—154·5° (Found: C, 74·1; H, 6·7; N, 9·0. Calc. for $C_{10}H_{11}ON$: C, 74·5; H, 6·9; N, 8·7%). Dimethyloxindole in acetic acid (distilled over chromium trioxide) absorbed 2·96 mols. of hydrogen at 19°/1 atm. over Adams's catalyst. *Hexahydro*-3 : 3-*dimethyloxindole* crystallised from ligroin in prisms, m. p. 126—127° (Found: C, 72·4; H, 9·9; N, 8·4. $C_{10}H_{17}ON$ requires C, 71·8; H, 10·2; N, 8·4%). One experiment was interrupted when 2·0 mols. of hydrogen had been absorbed, and the product, crystallised from ligroin or ethyl acetate, had the sharp and reproducible m. p. 99°; but, treated with aqueous solvents it gave dimethyloxindole (mixed m. p.). An equimolecular mixture of dimethyloxindole and the hexahydro-compound gave similar crystals from ligroin, m. p. and mixed m. p. 98—99°, and the 99° product showed ultra-violet absorption similar to that of dimethyloxindole.

cyclo*Hexane*spiro-3-*oxindole*.—Hexahydrobenzoic acid (3 g.) was heated with phenylhydrazine (3 g.) at 140° for 2 hr. and the product crystallised from ethanol and from benzene, giving plates, m. p. 171° (Found: N, 12·8. Calc. for $C_{13}H_{16}ON_2$: N, 12·8%). Hexahydrobenzophenylhydrazide was also prepared by the method of Rupe and Metz (*Ber.*, 1903, **36**, 1095), who give m. p. 164°. The hydrazide (2 g.) was heated with freshly ignited calcium oxide (8 g.) at 195° for 6 hr., the reaction being followed by titrating the evolved ammonia. The product was boiled for 1 hr. with concentrated hydrochloric acid, then filtered after cooling, and the solid residue continuously extracted with boiling ether. The brown, gummy extract was crystallised from ligroin and sublimed (130°; high vacuum), giving *cyclo*hexane*spiro*-3-oxindole, m. p. 121—122° (Found: C, 77·8; H, 7·6; N, 6·8. Calc. for $C_{13}H_{15}ON$: C, 77·6; H, 7·5; N, 7·0%). Moore and Plant (*J.*, 1951, 3477) give m. p. 124°. The same product was obtained (mixed m. p.) on oxidation of the zinc chloride complex of *cyclo*hexane*spiro*-3-indolenine (400 mg.) with potassium permanganate (500 mg.) in water (50 c.c.) containing potassium hydroxide (150 mg.) at 10°. After 6 hr. at 8—10° and 20 hr. at room temperature a little ethanol was added and the mixture boiled and filtered hot. The filtrate, saturated with carbon dioxide, was extracted with ether, yielding *cyclo*hexane*spiro*-3-oxindole (25 mg.) which was crystallised from ligroin.

2 : 3-cyclo*Heptenoindole*.—Hexahydrobenzaldehyde (Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 344) (3·7 g.) and pure phenylhydrazine (3·3 g.) were heated until reaction was complete and the red gum was dried in a vacuum. When this was heated with powdered zinc chloride (4 g.) a violent reaction occurred, and the product was steam-distilled with excess of sodium hydroxide solution. The volatile, pale yellow solid, sublimed and repeatedly crystallised from ligroin, formed colourless leaflets, m. p. 143—145°, alone or mixed with authentic 2 : 3-*cyclo*-

heptenoindole kindly supplied by Dr. S. G. P. Plant (Found : C, 84·3; H, 8·1; N, 7·6. Calc. for $C_{13}H_{15}N$: C, 84·2; H, 8·2; N, 7·6%). In acetic acid the *cyclo*heptenoindole gave with diazobenzenesulphonic acid a deep red azo-dye, changed to orange by alkali.

cyclo*Hexane*spiro-3-*indolenine*.—Hexahydrobenzaldehyde phenylhydrazone (2·5 g.) in a little ethanol was added to ethanol (5 c.c.) containing zinc chloride (7·5 g.) and refluxed in nitrogen for 3 hr. Addition of 2N-hydrochloric acid (15 c.c.) with ice (5 g.) gave, on shaking, a colourless solution over a sticky red gum. The dried gum was crystallised from ethanol, giving colourless plates of the zinc chloride *complex* of *cyclo*hexane*spiro*indolenine, m. p. 205·5° (previous softening) (Found : C, 61·8; H, 6·2. $C_{26}H_{30}N_2Cl_2Zn$ requires C, 61·6; H, 6·0%). The fragrant-smelling free base, liberated by potassium hydroxide and distilled in steam, boiled at 85°/20 mm. and gave no colour or precipitate with diazobenzenesulphonic acid.

The ultra-violet absorptions were determined with a Beckman spectrophotometer, on ethanolic solutions except in the case of bromo*allo*gelsemine hydrobromide which was dissolved in ethanol–water (2 : 3).

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480. *Some 6-Alkyl-5- and 7-Alkyl-8-aminoquinolines.*

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6- and 7-Alkylquinolines, as far as the butyl members, have been prepared from *p*- and *m*-alkylanilines by the Skraup reaction. Nitration converted the 6-alkylquinolines into 6-alkyl-5-nitroquinolines, but from the 7-alkyl compounds, besides 7-alkyl-8-nitroquinolines, minor products, probably 5-nitro-isomers, were isolated. A catalytic method of general usefulness was employed to reduce these products to 6-alkyl-5- and 7-alkyl-8-aminoquinolines. The picrates of the latter were noteworthy for their ability to retain up to three molecules of acetone in their crystals.

FOR work to be published later we required a number of compounds of the types named in the title. Recently (*J.*, 1953, 2066) we described the preparation of some *m*- and *p*-alkylanilines, and have now submitted these to the Skraup reaction. The resulting alkylquinolines were then nitrated and the products were reduced. In the Skraup reaction a *p*-alkylaniline can form only the 6-alkylquinoline, and the work of Bradford, Elliot, and Rowe (*J.*, 1947, 437) made it probable that the 7-alkylquinoline would be formed chiefly or exclusively from a *m*-alkylaniline. 6- and 7-Methylquinoline are well known, and Manske, Marion, and Leger (*Canad. J. Res.*, 1942, **20**, *B*, 133) reported the preparation of 7-ethylquinoline from *m*-ethylaniline but did not record its properties or establish its orientation. No other 6- or 7-alkylquinolines have been described previously.

Noelting and Trautmann (*Ber.*, 1890, **23**, 3654) prepared 6-methyl-8-nitroquinoline from 4-amino-3-nitrotoluene, and 8-hydroxy-7-methylquinoline from 3-amino-*o*-cresol (Me = 1). We found these reactions to be uncontrollably violent. Bradford *et al.* (*loc. cit.*) showed Skraup reactions to proceed satisfactorily when moderately dilute sulphuric acid was used, sodium *m*-nitrobenzenesulphonate being the oxidant. These conditions worked well in the two cases just mentioned, and were subsequently used in preparing 6-ethyl-, 6-butyl-, 7-butyl-, and 6-dodecyl-quinoline. Repetition of the Skraup reaction with *m*-ethylaniline, using the method described by Manske *et al.* (*loc. cit.*), showed it to work satisfactorily, although the yield of pure product was not so high as claimed by them. Their conditions have also been applied to the preparation of other compounds which we required, and the results allow some comparisons to be made between the two methods. The conditions described by the Canadian workers were unsuitable for the preparation of 6-dodecylquinoline, as charring occurred.

Noelting and Trautmann (*loc. cit.*) and Bogert and Fisher (*J. Amer. Chem. Soc.*, 1912, **34**, 1569), by nitrating 6-methylquinoline in sulphuric acid, obtained only 6-methyl-5-nitroquinoline. The products now similarly obtained from 6-ethyl-, -propyl-, -butyl-, and

-dodecyl-quinoline are regarded from analogy as the 5-nitro-compounds, and work to be described later justifies this assumption. The method used in working up the nitration solutions from the 6-alkylquinolines made unlikely the detection of minor products.

Tomisek, Graham, Griffith, Rose, and Christensen (*J. Amer. Chem. Soc.*, 1946, **68**, 1587) nitrated 7-methylquinoline in sulphuric acid, and proved the principal product to be 7-methyl-8-nitroquinoline. The same method has now been applied to 7-ethyl-, -propyl-, and -butyl-quinoline. The major product from 7-ethylquinoline has been proved (Ockenden and Schofield, unpublished work) to be 7-ethyl-8-nitroquinoline (thus proving the structure of 7-ethylquinoline also), and the same orientation is assumed in the other cases. Minor nitration products were also isolated from the ethyl and the butyl compound. Despite the suggestion implicit in the work of Capps (*J. Amer. Chem. Soc.*, 1947, **69**, 179), that 7-methylquinoline is to a small degree nitrated in the pyridine nucleus, a suggestion contrary to all known analogies (Schofield, *Quart. Reviews*, 1950, **4**, 393), we regard these minor isomers as 7-alkyl-5-nitroquinolines.

Reduction of 6-methyl-5-nitroquinoline with iron filings and dilute acetic acid, as described by Noelting and Trautmann (*loc. cit.*), although laborious was satisfactorily applied to the large scale. Preparation of 8-amino-7-methylquinoline with the same reagents, as described by Elderfield *et al.* (*J. Amer. Chem. Soc.*, 1946, **68**, 1524), was unsatisfactory. With some modification the method yielded 47% of the amine.

Several workers have reduced nitroquinolines to the amines by catalytic procedures (Capps, *loc. cit.*; *J. Amer. Chem. Soc.*, 1950, **72**, 4069; Rudy, *Ber.*, 1938, **71**, 847; Haskelberg, *J. Org. Chem.*, 1947, **12**, 434). Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1940, **62**, 1640) reduced 5- and 8-nitroquinoline using Adams' platinum oxide, and claimed that ethanol was an unsatisfactory solvent since sparingly soluble intermediate hydroxylamines were sensitive to hot alcohol. This statement is not wholly consistent with the experiments which they describe. Our attempts to repeat this work failed. Reduction to the hydroxylamine (which separated) occurred rapidly, but reduction then ceased. The same workers claimed the rapid reduction of 8-nitroquinoline in a mixture of ethyl acetate, ethanol, and ether, but we found this reaction to need several days. This was also the case with 7-methyl-8-nitroquinoline under these conditions, and here separation of the green hydroxylamine was also observed.

Finally we found that a modification of the method used by Langenbeck, Juttermann, and Hellrung (*Annalen*, 1932, **499**, 201) for reducing 5-nitroquinoline was generally applicable to nitroquinolines. In relatively dilute methanolic solution, with 5% palladium–charcoal, reduction was rapid, no intermediate compound separated, and the pure amine was easily isolated. By this method the 6-alkyl-5- and 7-alkyl-8-nitroquinolines described above were all successfully converted into the corresponding amines.

The 6- and 7-alkylquinolines were very pale yellow, highly refractive oils, the b. p.s of which increased as the series was ascended. The 6-alkylquinoline picrates showed a lower m. p. than the 7-isomers, m. p.s in both series decreasing as the series was ascended. 7-Alkyl-8-nitroquinolines melted at higher temperatures than the 6-isomers; in each series the m. p. fell with increasing size of the alkyl group. Only 6-butyl- and 6-dodecyl-5-nitroquinoline appeared to form stable hydrates. The aminoquinolines were prone to form hydrates, a property which rendered the criterion of constant m. p. of little value as a test for purity. Because of hydrate formation the m. p.s of the 6-alkyl-5-aminoquinolines showed no definite trend, but in the 7-alkyl series they decreased as the series was ascended, 8-amino-7-ethyl-, -7-propyl-, and -7-butyl-quinoline being liquids. The amino-alkylquinolines formed highly crystalline picrates. Those derived from 7-alkyl-8-aminoquinolines crystallised normally from methanol, but from acetone formed bright scarlet crystals which retained up to three molecules of the solvent. 6-Alkyl-5-aminoquinoline picrates did not possess this property.

Experimental

Extracts were dried with anhydrous sodium sulphate.

Skraup Reactions.—(*a*) The amine, glycerol, sodium *m*-nitrobenzenesulphonate, and sulphuric acid (75% w/w) were stirred under gentle reflux. After being set aside overnight the mixture was diluted, treated with excess of sodium nitrite, and then boiled. The mixture was

rendered strongly alkaline and steam-distilled, except in the case of 6-butyl- and 6-dodecylquinoline, which were extracted with ether, and of 6-methyl-8-nitroquinoline which separated as a solid and was collected. The distillates were extracted with ether and the oils recovered from the extracts were distilled. In the case of 8-hydroxy-7-methylquinoline the Skraup reaction mixture was basified, acidified with acetic acid, and then treated with excess of ammonia. Steam-distillation and addition of aqueous ammonia to the distillate gave the pure product. Results are in Table 1.

(*b*) The amine, boric acid, ferrous sulphate, *o*-nitrophenol, glycerol, and concentrated sulphuric acid were refluxed together. After being kept overnight the mixture was processed as in (*a*). Results are in Table 2. The stated yield of 7-propylquinoline is of doubtful significance since the starting amine was impure.

The properties of the *quinolines* prepared in (*a*) and (*b*), and of their picrates, are recorded in Table 3.

TABLE 1.

Quinoline	Starting amine (g.)	75% w/w H_2SO_4 (g.)	Sodium *m*-nitrobenzenesulphonate (g.)	Glycerol (g.)	Temp.	Time (hr.)	Yield (%) (pure)
8-Hydroxy-7-methyl ...	5	40	10	18·8	120—125°	8	54
6-Methyl-8-nitro	105	500	200	125	140	9	73
6-Ethyl	30	165	75	42·5	130—140	,,	75
6-Butyl	52	250	100	72·5	,,	11·5	82
7-Butyl	18·4	90	35	22	140	12	70
6-Dodecyl	54·7	150	60	23	150—160	10	56

TABLE 2.

Quinoline	Starting amine (g.)	$FeSO_4$ (g.)	H_3BO_3 (g.)	*o*-Nitrophenol (g.)	Glycerol (g.)	Conc. H_2SO_4 (c.c.)	Time (hr.)	Yield (pure) (%)
8-Hydroxy-7-methyl	5	1·8	3·3	4·2	18·8	9	6	32
6-Ethyl	24	7·2	13	16·4	75	36	7·5	82
7-Ethyl	36	10·5	19·5	24·9	82·5	54	,,	74
6-Propyl	31	,,	,,	,,	112·5	,,	8	68
7-Propyl	10	6	11	14	64	30	14	45
6-Butyl	39·5	8·7	16·3	20·8	93·7	45	10·5	82
7-Butyl	10	2·5	4·5	6	26	13	6	64·5

TABLE 3. 6- *and* 7-*Alkylquinolines obtained by Skraup reactions.*

No.	Quinoline	B. p. (°/mm.)	n^a	Formula	Found (%): C	Found (%): H	Reqd. (%): C	Reqd. (%): H	Picrate: Form [b]	Picrate: M. p.	Picrate: Solvent
1	6-Ethyl	140—142/12	1·6012	$C_{11}H_{11}N$	83·2	7·0	84·0	7·05	Needles	200—201	Aq. $COMe_2$
2	7-Ethyl	128—129/6	1·6012	—	—	—	—	—	,,	231—233 [c]	MeOH–$COMe_2$
3	6-Propyl	140/7	1·5878	$C_{12}H_{13}N$	84·4	8·1	84·2	7·7	,,	171—172	,,
4	7-Propyl	145—147/7	1·5900	,,	84·0	7·9	,,	,,	,,	191—193	,,
5	6-Butyl	161—164/12	1·5802	$C_{13}H_{15}N$	85·5	8·3	84·3	8·2	Prisms	162	MeOH
6	7-Butyl	152—154/6	1·5828	,,	83·7	8·1	,,	,,	Needles	180	$COMe_2$
7	6-Dodecyl	196—198/0·5	1·5345	$C_{21}H_{31}N$	84·9	10·3	84·75	10·5	Flakes	131	MeOH

Picrate 1. Found: C, 53·1; H, 3·7. $C_{11}H_{11}N,C_6H_3O_7N_3$ requires C, 52·9; H, 3·65%.
,, 3. ,, C, 54·0; H, 3·9. $C_{12}H_{13}N,C_6H_3O_7N_3$,, C, 54·0; H, 4·0%.
,, 4. ,, C, 53·7; H, 3·8. ,, ,, ,, ,, ,,
,, 5. ,, C, 55·1; H, 4·3. $C_{13}H_{15}N,C_6H_3O_7N_3$,, C, 55·05; H, 4·4%.
,, 6. ,, C, 55·3; H, 4·4. ,, ,, ,, ,, ,,
,, 7. ,, C, 61·2; H, 6·6. $C_{21}H_{31}N,C_6H_3O_7N_3$,, C, 61·6; H, 6·5%.

[a] Determined by daylight. The high viscosity of the liquids made it difficult to obtain closely reproducible values for this constant. [b] All yellow. [c] Manske *et al.* (*loc. cit.*) gave m. p. 229°.

Nitrations.—(a) 6-*Alkylquinolines.* The quinoline in concentrated sulphuric acid was treated, whilst being stirred, with a solution of nitric acid (*d* 1·42) in concentrated sulphuric acid, the temperature being kept below 5° (below 0° for 6-dodecylquinoline to prevent oxidation). The nitration solution was poured on ice (with 6-dodecylquinoline this precipitated the hydrated nitro-compound); the product precipitated by neutralisation with sodium carbonate was collected and recrystallised. When the nitration solution from 6-butylquinoline was poured on ice and water (1·5 l.) a yellow precipitate was obtained, only partly soluble in organic solvents. This mixture of the nitro-compound and its nitrate was triturated with ammonia, and the

resulting solid was combined with that obtained by basifying the mother-liquor. The total product was dried *in vacuo*, a dark brown oil resulting. The yield of this material is recorded below. When exposed to the atmosphere this oil was transformed into clusters of stout, pale yellow needles of *6-butyl-5-nitroquinoline hemihydrate*, m. p. 35—37° (Found: C, 64·9; H, 5·9. $C_{13}H_{14}O_2N_2,\frac{1}{2}H_2O$ requires C, 65·2; H, 6·3%).

(b) *7-Alkylquinolines.* The method was similar to that described in (*a*) except that fuming nitric acid was the nitrating agent. In all cases dilution of the nitration solution precipitated the main bulk of the product, which was collected and recrystallised. The acid mother-liquors from 7-ethyl- and -butyl-quinoline were neutralised with aqueous ammonia, and the product was either collected (ethyl) or extracted with chloroform (butyl). Both compounds were crystallised from aqueous methanol. *7-Ethyl-5(?)-nitroquinoline* gave soft pale yellow plates, m. p. 47—49° (Found: C, 65·4; H, 5·4. $C_{11}H_{10}O_2N_2$ requires C, 65·3; H, 5·0%), and *7-butyl-5(?)-nitroquinoline* crisp yellowish-brown plates, m. p. 73—74° (Found: C, 66·5; H, 6·0. $C_{13}H_{14}O_2N_2,\frac{1}{4}H_2O$ requires C, 66·5; H, 6·2%). The *picrate* from the former compound formed soft yellow plates, m. p. 126—127° (Found: C, 46·4; H, 3·4. $C_{11}H_{10}O_2N_2,C_6H_3O_7N_3$ requires C, 47·3; H, 3·0%), and from the latter, clusters of bright yellow needles, m. p. 129° (Found: C, 49·7; H, 3·7. $C_{13}H_{14}O_2N_2,C_6H_3O_7N_3$ requires C, 49·7; H, 3·7%), from methanol–ether.

The results and *products* of these nitrations are in Table 4.

TABLE 4.

Quinoline in	conc. H_2SO_4 (g.)	conc. H_2SO_4 (c.c.)	Fuming H_2SO_4 (c.c.)	HNO_3 (c.c.)	Fuming nitric acid (c.c.)	Recrystd. from *	Pure product (g.)	Pure product (%)
6-Methyl ...	220	550	200	125	—	$COMe_2$	217	75
7-Methyl ...	80	200	—	—	32	,,	76	72
6-Ethyl ...	40	105	25	20	—	Et_2O–Pet	45	85
7-Ethyl ...	16	45	—	—	7·5	Aq. $COMe_2$	13	63
6-Propyl ...	26·7	67	17	13·5	—	Pet	31	92
7-Propyl ...	3·7	10	—	—	1·5	,,	3·1	65
6-Butyl ...	42	100	70	22	—	—	44	84
7-Butyl ...	15·5	40	—	—	6·0	Et_2O–Pet	13·7	71
6-Dodecyl	35	175	54	12	—	Aq. MeOH	30·6	74

* Pet = light petroleum.

Quinoline Alkyl	NO_2	M. p.	Form	Found (%): C	Found (%): H	Formula	Reqd. (%): C	Reqd. (%): H
6-Me	5	116—117°	—	—	—	—	—	—
7-Me	8	183—184	—	—	—	—	—	—
6-Et	5	52—53	Prisms	65·7	4·9	$C_{11}H_{10}O_2N_2$	65·3	5·0
7-Et	8	136	Needles	65·2	4·85	,,	,,	,,
6-Pr	5	23—25	Plates	66·75	5·4	$C_{12}H_{12}O_2N_2$	66·65	5·6
7-Pr	8	58—59	Needles	66·5	5·7	,,	,,	,,
6-Bu	5	†	—	—	—	—	—	—
7-Bu	8	71	,,	67·6	6·1	$C_{13}H_{14}O_2N_2$	67·8	6·1
6-$C_{12}H_{25}$	5	53—55	,,	70·1	8·9	$C_{21}H_{30}O_2N_2,H_2O$	70·0	8·95

† The anhydrous product is an oil, b. p. 128°/0·2 mm. For the hydrate see text.

Alkylaminoquinolines.—(a) *5-Amino-6-methylquinoline.* The nitro-compound (152 g.) in acetic acid (200 c.c.) and water (3·5 l.) was stirred with iron pin dust (100 g.) at 95° for 9—10 hr. The mixture was filtered, the filtrate was basified with ammonia, and the dark green product was crystallised from boiling water. The iron residues were extracted with boiling water to afford a further quantity of material. 5-Amino-6-methylquinoline (103 g., 80%) separated from water as green needles, m. p. 135° (Bogert and Fisher, *loc. cit.*, gave m. p. 135°. Noelting and Trautmann, *loc. cit.*, gave m. p. 145°). Recrystallisation from ethanol changed the m. p. to 75—85°. The product produced by catalytic reduction in methanol (see below) had an indefinite m. p., softening at 70°, and finally melting at 90—93°.

(b) *8-Amino-7-methylquinoline.* 7-Methyl-8-nitroquinoline (20 g.), etched pin dust (20 g.), acetic acid (40 c.c.), and water (200 c.c.) were stirred at 95° for 24 hr. By basification of the filtrate from this mixture a wet sludge was obtained which was extracted several times with boiling acetone. The iron residues were similarly treated, and the combined extracts were diluted with ether, separated from an aqueous layer, and dried. The product isolated by removal of the solvent was distilled, giving a fraction, b. p. 154—156°/6—8 mm., m. p. 40—45°. Crystallisation from aqueous alcohol gave yellow needles, m. p. 41—44°. On exposure of this solid to the atmosphere the m. p. changed to 58—59° (cf. Elderfield *et al.*, and Capps, *locc. cit.*).

(c) *Catalytic reductions.* The nitroquinoline, 5% palladium–charcoal, and methanol were shaken with hydrogen at atmospheric pressure. When reduction was complete the catalyst was removed and the solution was concentrated. Solid amines were precipitated by water, but oils were distilled. The details are in Table 5. The following data refer to the products.

(1) *5-Amino-6-methylquinoline picrate*, orange-red needles, m. p. 225—227° (decomp.) (Found: C, 49·7; H, 3·6. $C_{10}H_{10}N_2,C_6H_3O_7N_3$ requires C, 49·6; H, 3·4%).

(2) *8-Amino-7-methylquinoline hemihydrate* (Found: C, 72·2; H, 6·4. $C_{10}H_{10}N_2,\frac{1}{2}H_2O$ requires C, 71·8; H, 6·6%), greenish-yellow needles from aqueous methanol. *Picrate*, orange-yellow needles, m. p. 224—226° (Found: C, 49·7; H, 3·4%), from methanol, or scarlet needles, m. p. 200—220° (decomp.) (Found: C, 53·1; H, 3·8. $C_{10}H_{10}N_2,C_6H_3O_7N_3,2C_3H_6O$ requires C, 52·5; H, 5·0. $C_{10}H_{10}N_2,C_6H_3O_7N_3,3C_3H_6O$ requires C, 53·5; H, 5·6%), from acetone.

(3) *5-Amino-6-ethylquinoline hydrate* (Found: C, 69·75; H, 7·5. $C_{11}H_{12}N_2,H_2O$ requires C, 69·4; H, 7·4%), greenish-yellow blades from aqueous methanol. *Picrate*, reddish-orange needles, m. p. 220—222° (Found: C, 49·7; H, 3·6. $C_{11}H_{12}N_2,C_6H_3O_7N_3$ requires C, 50·8; H, 3·8%), from methanol.

(4) *8-Amino-7-ethylquinoline* (Found: C, 75·8; H, 7·0. $C_{11}H_{12}N_2$ requires C, 76·7; H, 7·0%), yellow oil. The *hydrated* amine (Found: C, 74·2; H, 6·5. $C_{11}H_{12}N_2,\frac{1}{4}H_2O$ requires C, 74·7; H, 7·1%) gave prisms from light petroleum (b. p. 40—60°). *Picrate*, orange needles, m. p. 203—204° (Found: C, 51·7; H, 3·8%) from methanol, or scarlet prisms, m. p. 180° (Found: C, 52·6; H, 4·1. $C_{11}H_{12}N_2,C_6H_3O_7N_3,C_3H_6O$ requires C, 52·3; H, 4·2%), from acetone.

(5) *5-Amino-6-propylquinoline hydrate* (Found: C, 69·9; H, 7·9. $C_{12}H_{14}N_2,H_2O$ requires C, 70·55; H, 7·9%), felted needles from aqueous methanol. *Picrate*, crimson prisms, m. p. 227° (decomp.) (Found: C, 52·4; H, 4·2. $C_{12}H_{14}N_2,C_6H_3O_7N_3$ requires C, 52·1; H, 4·1%), from methanol.

TABLE 5.

			MeOH	Pd–C	Pure product			
No.	Quinoline	(g.)	(c.c.)	(g.)	g.	%	B. p. (°/mm)	M. p.[a]
1	6-Methyl-5-nitro	4	100	1	3·3	98	—	(90—93°) 135°
2	7-Methyl-8-nitro	20	550	2	16·3	97	156/6	(41—44) 58—59
3	6-Ethyl-5-nitro	,,	400	,,	15·5	91	—	(88) 104
4	7-Ethyl-8-nitro	12·9	420	1·5	10·7	98·5	167—168/8	32—35
5	5-Nitro-6-propyl	18	450	2	15·2	98	—	(69—73) 87—90
6	8-Nitro-7-propyl	2·3	50	0·2	2	100	180—182/10	5—10
7	6-Butyl-5-nitro	27·5	450	1·3	24·5	100	—	(55—60) 85—86
8	7-Butyl-8-nitro	10	250	1	8·55	98·2	177—178/6	14—15
9	6-Dodecyl-5-nitro	7	360	,,	6·1	95·5	—	67—69

[a] M. p.s in parentheses refer to unhydrated or lower hydrated forms.

(6) *8-Amino-7-propylquinoline* (Found: C, 77·3; H, 7·6. $C_{12}H_{14}N_2$ requires C, 77·4; H, 7·6%), yellow oil at room temperature. The m. p. is approximate. *Picrate*, scarlet prisms, m. p. 197—199° (decomp.) (Found: C, 52·1; H, 3·9%), from methanol, or bright scarlet prisms, m. p. 163° (Found: C, 54·8; H, 4·7. $C_{12}H_{14}N_2,C_6H_3O_7N_3,3C_3H_6O$ requires C, 55·0; H, 5·9%), from acetone.

(7) *5-Amino-6-butylquinoline hydrate* (Found: C, 70·9; H, 8·0. $C_{13}H_{16}N_2,H_2O$ requires C, 71·5; H, 8·3%), soft pale green prisms from aqueous methanol. *Picrate*, orange needles, m. p. 218—220° (decomp.) (Found: C, 53·6; H, 4·6. $C_{13}H_{16}N_2,C_6H_3O_7N_3$ requires C, 53·2; H, 4·5%), from methanol.

(8) *8-Amino-7-butylquinoline* (Found: C, 78·5; H, 8·15. $C_{13}H_{16}N_2$ requires C, 77·9; H, 8·05%). *Picrate*, orange needles, m. p. 172—173° (Found: C, 53·65; H, 4·0%), from methanol, or orange crystals, m. p. 127—128° (Found: C, 55·1; H, 4·65. $C_{13}H_{16}N_2,C_6H_3O_7N_3,2C_3H_6O$ requires C, 55·0; H, 4·7%), from acetone.

(9) *5-Amino-6-dodecylquinoline hemihydrate* (Found: C, 77·8; H, 9·8. $C_{21}H_{32}N_2,\frac{1}{2}H_2O$ requires C, 78·4; H, 10·3%), light brown prisms from aqueous methanol. *Picrate*, red-orange needles, m. p. 130° (Found: C, 60·0; H, 6·5. $C_{21}H_{32}N_2,C_6H_3O_7N_3$ requires C, 59·8; H, 6·5%), from methanol.

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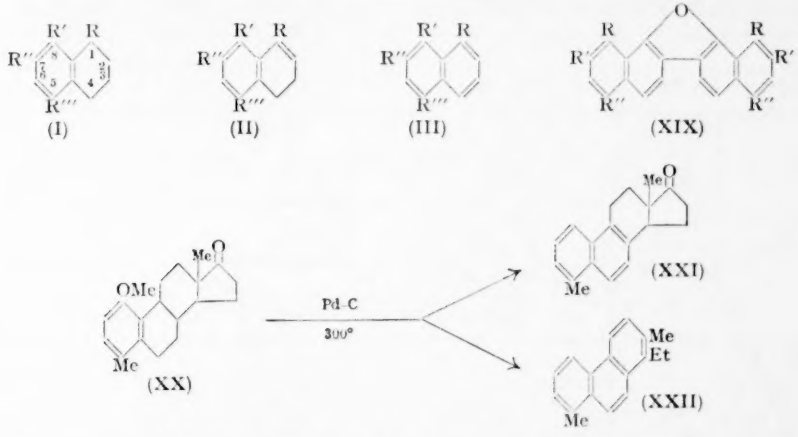
481. *The Elimination of Non-angular Alkyl Groups in Aromatisation Reactions. Part II.**

By Wesley Cocker, Brian E. Cross, J. T. Edward, D. S. Jenkinson, and (Miss) Joan McCormick.

Further examples of the loss of alkyl groups from tetrahydronaphthalenes of type (I; R = R′ = alkyl; or R = alkyl and R′ = OMe), when dehydrogenated with palladised charcoal and selenium, have been encountered (cf. Cocker, Cross, and McCormick, *J.*, 1952, 72). It has been shown that the ethyl group is eliminated as ethyl hydrogen selenide when selenium is the dehydrogenating agent. Two examples of the loss of methyl are described.

In Part I * of this series it was shown that in the reaction of tetralins of type (I; R = Et, R′ = R″ = R‴ = H; R = R′ = R″ = R‴ = Me; R = Et, R′ = H, R″ = R‴ = Me) with sulphur, selenium, or palladised charcoal, normal aromatisation proceeds, yielding compounds of type (III; R = alkyl). In systems such as (I; R = Et, R′ = R″ = R‴ = Me; R = Et, R′ = R‴ = Me, R″ = H; R = Et, R′ = Me, R″ = H, R‴ = OMe), however, dehydrogenation with selenium leads to loss of the ethyl group, and production of compounds of type (III; R = H). Similar results were experienced with the corresponding dihydro-compounds (II). The work has been extended, and the results are summarised in the annexed Table.

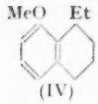
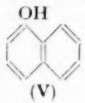
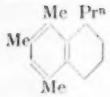
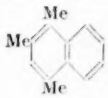
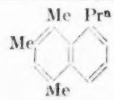
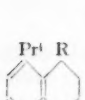
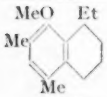
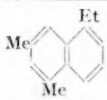
From the Table the following conclusions may be drawn. (*a*) Under normal conditions of use, sulphur is a " safe " catalyst; all alkyl groups are retained. It must be admitted that the number of examples of its use is small. At temperatures above 250°, or if an excess of sulphur is used, intractable products are produced. (*b*) No example of the loss



of ethyl was encountered when palladised charcoal was used at 260—280°, but at 330—350° (I; R = Et, R′ = R″ = R‴ = Me) partly loses its ethyl group (cf. Part I, *loc. cit.*), and the *n*-propyl group is partly eliminated from the system (VI) at 260—280°. On the other hand, in (IX; R = Me or Et, R′ = Pr^{i}), the *iso*propyl group is eliminated from the aromatic ring when palladised charcoal is the catalyst; we were unable to prepare the tetralin (I; R = Pr^{i}, R′ = Me). This catalyst is also capable of removing methoxyl. Thus, the ether (XVII) yields the hydrocarbon (XVIII), and it has been shown † that the methoxy-compound (XX) yields a mixture of the methoxyl-free compounds (XXI) and (XXII) on dehydrogenation with palladised charcoal at 300° for twenty minutes. Cocker *et al.* (*J.*, 1950, 1781) further have shown that 1-ethyl-1 : 2 : 3 : 4-tetrahydro-5-methoxy-7 : 8-dimethylnaphthalene affords 8-ethyl-1 : 2-dimethylnaphthalene with palladised

* Part I, *J.*, 1952, 72. † Personal communication from Dr. Andre Dreiding, Detroit.

charcoal. (*c*) Selenium removes ethyl or larger groups from $C_{(1)}$ in systems of type (I; R = Et or Pr, R′ = Me). There is insufficient evidence to show whether *iso*propyl is eliminated from $C_{(8)}$ in systems where there is an ethyl group at $C_{(1)}$, although the odour of

Reactant	Product obtained by using: Selenium (330—350°)	Palladised charcoal (260—280°)	Sulphur (230—240°)
 (IV)	 (V) After demethylation		
 (VI)	 (VII)	(VII) + (VIII)	 (VIII)
 (IX) R = Me	Mixture; (XI) isolated	(X)	(XI)
R = Et	Intractable mixture	(XII)	(XIII)
(XIV) R = Me	(XV)	(XV)	
R = Et	(XVI)	Not aromatised	Not aromatised
 (XVII)		 (XVIII)	
(I; R = Et; R′ = R″ = R‴ = Me)		330—350°. Mixture; (III; R = H; R′ = R″ = R‴ = Me) isolated	

alkyl selenide indicates loss of alkyl; but in the system where ethyl groups are at $C_{(1)}$ and $C_{(8)}$, it is the 1-ethyl which is eliminated: (XIV; R = Et) ⟶ (XVI).

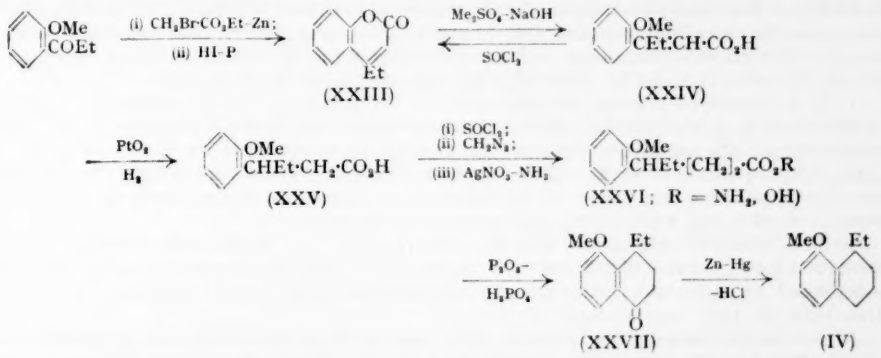
Two examples of loss of non-angular methyl groups have been encountered during dehydrogenation with selenium. Thus, 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene affords 5′ : 5″-dimethyldinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = H, R″ = Me), along with the expected 5 : 8-dimethyl-1-naphthol. Under similar conditions 1 : 2 : 3 : 4-tetrahydro-5 : 7 : 8-trimethyl-1-oxonaphthalene yields 5 : 7-dimethyl-1-

naphthol and 5′ : 5″-7′ : 7″ : 8′ : 8″-hexamethyldinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = R″ = Me). The dimethyldinaphthofuran (XIX; R = R′ = H, R″ = Me) has not been synthesised by an unambiguous method but there can be little doubt of its structure. Thus, the analogous tetramethylfuran (XIX; R = H, R′ = R″ = Me) is obtained when 1 : 2 : 3 : 4-tetrahydro-5 : 7-dimethyl-1-oxonaphthalene is heated with selenium, and this furan is the product of dehydrogenation of 5 : 7-dimethyl-1-naphthol with vanadium pentoxide (cf. Clemo, Cockburn, and Spence, *J.*, 1931, 1265). Further, the three furans mentioned, and dinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (XIX; R = R′ = R″ = H) (Clemo, Cockburn, and Spence, *loc. cit.*) have similar light-absorption characteristics, with appropriate changes due to the number and position of the alkyl groups. From past experience we have no reason to believe that 5 : 7 : 8-trimethyl-1-naphthol could yield 5 : 7-dimethyl-1-naphthol on dehydrogenation; it is much more likely that bis-5 : 7 : 8-trimethyl-1-naphthyl ether is the precursor of the dimethylnaphthol.

We have investigated the by-products in the aromatisation of (I; R = Et, R′ = R″ = R‴ = Me) with selenium; it has been found that the ethyl group eliminated is converted into ethyl hydrogen selenide in at least 60% of the theoretical quantity; no dialkyl selenide was encountered. Losses in manipulation probably account for the remainder, since although we were unable to analyse the gaseous products for paraffins, no olefin was produced. At least 70% of the theoretical quantity of hydrogen selenide was trapped as its lead salt.

It is difficult to see why the ethyl and *n*-propyl groups should be, in general, eliminated from systems such as (I; R = Et, R′ = R″ = R‴ = Me), whereas in similar systems where R = Me the group is retained. Models show that there is little interference between *n*-alkyl, and even *iso*propyl, groups at $C_{(1)}$ and $C_{(8)}$ in either the tetralin or the naphthalene. It may be that loss of ethyl proceeds via the ethylidene group, which could yield ethyl hydrogen selenide on attack by selenium. At the same time it must be remembered that 1-ethyltetralin (I; R = Et, R′ = R″ = R‴ = H) is unaffected by selenium (Cocker, Cross, and McCormick, *loc. cit.*).

The tetralins of type (I) were made by conventional methods, with the exception of (IV), for which the route shown was employed. A number of interesting points emerge



from this synthesis. It was found that the hydroxy-ester obtained in the Reformatsky reaction between *o*-methoxypropiophenone and ethyl bromoacetate could not be dehydrated in the usual way, but with hot hydriodic acid 4-ethylcoumarin (XXIII) was obtained in fair yield. The unsaturated acid (XXIV) did not give an acid chloride with thionyl chloride, but afforded 4-ethylcoumarin instead. An analogy to this is the reaction between benzoyl chloride and phenetole, in which ethyl benzoate is produced. Cyclisation of the acid (XXVI; R = OH) was difficult, as might be expected since ring-closure *meta* to methoxyl is involved (cf. Johnson, "Organic Reactions," John Wiley and Sons, Inc., 1944, Vol. II, p. 120). Of the many reagents employed, in conjunction with either the

acid or its chloride, polyphosphoric acid (cf. Birch, Jaeger, and Robinson, *J.*, 1945, 582) was the only one to effect cyclisation in resonable yield.

Attempts to prepare (I; R = Pr^i, R′ = R‴ = Me, R″ = H) were unsuccessful. When 1 : 2 : 3 : 4-tetrahydro-5 : 8-dimethyl-1-oxonaphthalene (Barnett and Sanders, *J.*, 1933, 434) was condensed with *iso*propylmagnesium bromide in ether, the product consisted of a mixture of unchanged tetralone, and its reduction product, the tetralol. In boiling anisole, the product obtained gave analyses as a mixture of the required *iso*propyl compound (II; R = Pr^i, R′ = R‴ = Me; R″ = H) and (II; R = R″ = H, R′ = R‴ = Me). After hydrogenation, followed by dehydrogenation with selenium, 1 : 4-dimethylnaphthalene was obtained, with only a slight odour of alkyl selenide. Further efforts to prepare the required tetralin involved the following reactions: tetralone $\xrightarrow{LiAlH_4}$ tetralol $\xrightarrow{HBr}$ bromotetralin (I; R = Br, R′ = R‴ = Me, R″ = H). The last compound formed a Grignard solution, but this failed to react with *iso*propyl bromide.

Two cases of loss of alkyl group were encountered, other than during dehydrogenation. Thus, bromination of 1 : 2 : 3 : 4-tetrahydro-1 : 5-dimethyl-8-*iso*propylnaphthalene gave a tribromo-compound with loss of the *iso*propyl group. Again 2-*tert.*-butyl-5-methylanisole reacted with succinic anhydride and aluminium chloride in methylene chloride to give β-(4-methoxy-2-methylbenzoyl)propionic acid.

Experimental

Unless otherwise stated, the standard conditions for dehydrogenation were as follows: (1) *Palladised charcoal.* Equal weights of catalyst and hydrocarbon were heated together at 260—280° for 4—4·5 hr. (2) *Selenium.* Three parts of this reagent and one part of hydrocarbon were heated together at 330—350° for 4 hr. (3) *Sulphur.* Theoretical quantities of both reagents were heated together at 220—240° for 3 hr. All hydrocarbons were distilled from sodium before analysis.

1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethyl*-1-n-*propylnaphthalene* (VI) *and* 1 : 2-*Dihydro*-5 : 6 : 8-*trimethyl*-4-n-*propylnaphthalene.*—The corresponding tetralone (cf. Cocker, Cross, and McCormick, *loc. cit.*) (10·7 g.) in ether (70 c.c.) was added to a Grignard solution from *n*-propyl bromide (31·1 c.c.) and magnesium (8·3 g.) in ether (80 c.c.), and the mixture refluxed for 1 hr. and set aside overnight. After decomposition, the *dihydro*-compound (9·2 g.) was obtained as an oil, b. p. 170—172°/20 mm. (Found: C, 88·0; H, 10·15. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%). The *tetrahydro*-compound (VI) was produced as an oil (4·7 g.), b. p. 170—172°/6 mm., when the preceding compound was reduced in acetic acid (40 c.c.) over palladised charcoal (0·8 g.). The oil slowly solidified, and crystallised from methyl alcohol–ether as plates, m. p. 45—46° (Found: C, 88·6; H, 11·0. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

1 : 3 : 4-*Trimethyl*-5-n-*propylnaphthalene* (VIII).—The tetralin (0·9 g.), heated with sulphur, yielded an oil, b. p. 158°/15 mm., which was converted into its *picrate* (0·45 g.), m. p. 76°. This crystallised as dark red needles (from methyl alcohol), m. p. 81—82° (Found: C, 59·2; H, 5·2. $C_{22}H_{29}O_7N_3$ requires C, 59·9; H, 5·2%). 1 : 3 : 4-*Trimethyl*-5-n-*propylnaphthalene* was obtained from the picrate as a pale yellow oil, but there was too little for an accurate b. p. to be taken (Found: C, 90·6; H, 9·5. $C_{16}H_{20}$ requires C, 90·6; H, 9·4%).

1 : 2 : 4-*Trimethylnaphthalene.*—The above tetralin (0·7 g.), heated with selenium, yielded an oil (0·44 g.; b. p. 150—153°/5 mm.). From the oil (0·1 g.), a picrate (0·12 g.), m. p. 146—148° undepressed by authentic 1 : 2 : 4-trimethylnaphthalene (Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140), was obtained.

1 : 5-*Dimethyl*-4-iso*propylnaphthalene* (XI) *and* 1 : 2 : 3 : 4-*Tetrahydro*-1 : 5-*dimethyl*-8-iso*propylnaphthalene* (IX; R = Me).—β-(2-Methyl-5-*iso*propylbenzoyl)propionic acid (Muhr, *Ber.*, 1895, **28**, 3217; Dev and Guha, *J. Indian Chem. Soc.*, 1948, **25**, 315) was orientated by oxidation with hypochlorite to 2-methyl-5-*iso*propylbenzoic acid (Bogert and Tuttle, *J. Amer. Chem. Soc.*, 1916, **38**, 1353), and characterised as its amide. The required 1 : 2 : 3 : 4-tetrahydro-5-methyl-1-oxo-8-*iso*propylnaphthalene was then prepared as described by Dev and Guha.

This tetralone (8·8 g.) with methylmagnesium iodide gave 1 : 2-*dihydro*-4 : 8-*dimethyl*-5-iso*propylnaphthalene* as an oil (6·6 g.), b. p. 129·5—132·5°/10 mm. (Found: C, 89·8; H, 10·2. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

1 : 2 : 3 : 4-*Tetrahydro*-1 : 5-*dimethyl*-8-iso*propylnaphthalene* (IX; R = Me) was obtained as an oil (3·2 g.), b. p. 131—135°/8 mm. (Found: C, 88·95; H, 10·9. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%), when the previous compound (5·3 g.) was reduced in acetic acid over Adams catalyst.

It gave, with loss of the *iso*propyl group, a *tribromo*-compound (not orientated), m. p. 104° (leaflets from alcohol) (Found: C, 36·4, 36·7; H, 3·0, 3·3; Br, 60·0. $C_{12}H_{13}Br_3$ requires C, 36·3; H, 3·3; Br, 60·45%).

The tetrahydro-compound (0·6 g.), dehydrogenated with sulphur, gave an oil (0·4 g.), b. p. 110—114°/6 mm., which was converted into its *picrate*. This separated from methyl alcohol in orange needles, m. p. 132—133° (Found: C, 59·3; H, 4·9. $C_{21}H_{21}O_7N_3$ requires C, 59·0; H, 4·9%). Decomposition of the picrate with ammonia yielded 1 : 5-*dimethyl*-4-iso*propylnaphthalene* (XI), b. p. 95°/6 mm. (Found: C, 90·8; H, 8·9. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%).

Dehydrogenation of the tetrahydro-compound (2·5 g.) with palladised charcoal gave an oil (1·53 g.), b. p. 115—120°/5 mm., which slowly solidified. Crystallisation from methyl alcohol–ether yielded 1 : 5-dimethylnaphthalene (X; 0·5 g.), m. p. 80—82° (cf. "Elsevier's Encyclopaedia of Organic Chemistry," 1948, Vol. XIIB, p. 136), characterised as its picrate, m. p. 138—139° (Elsevier, *op. cit.*), and its *styphnate* (yellow needles from methyl alcohol), m. p. 156—158° (Found: C, 54·0; H, 3·75. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·75%).

4-*Ethyl*-1 : 2-*dihydro*-8-*methyl*-5-iso*propylnaphthalene*.—1 : 2 : 3 : 4-Tetrahydro-5-methyl-1-oxo-8-*iso*propylnaphthalene (6·72 g.), reacting with ethylmagnesium iodide from magnesium (4·85 g.) and ethyl iodide (16 c.c.), yielded the required *dihydro*-compound (6 g.), b. p. 130—135°/6 mm. (Found: C, 89·5; H, 10·3. $C_{16}H_{22}$ requires C, 89·7; H, 10·3%).

1-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methyl*-8-iso*propylnaphthalene* (IX; R = Et).—The dihydro-compound (3·36 g.), reduced in acetic acid (20 c.c.) over Adams's catalyst (100 mg.), yielded the *tetralin* (2·42 g.), b. p. 130—135°/7 mm. (Found: C, 88·3; H, 10·8. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

Picrate of 1-*Ethyl*-5-*methylnaphthalene* (XII).—The preceding compound (0·7 g.), heated with palladised charcoal, gave an oil (0·6 g.), which was converted into its picrate (0·9 g.; m. p. 64—80°). Crystallised thrice from methyl alcohol, it had m. p. 97—98° (Harvey, Heilbron, and Wilkinson, *J.*, 1930, 423, give m. p. 97°), depressed by picrates of 1-methyl-4-*iso*propyl- (Ruzicka and Mingazzini, *Helv. Chim. Acta*, 1922, **5**, 710), and 5-ethyl-1-methyl-4-*iso*propyl-naphthalene (XIII).

5-*Ethyl*-1-*methyl*-4-iso*propylnaphthalene* (XIII).—The tetralin (IX; R = Et) (0·5 g.), dehydrogenated with sulphur, afforded an oil (0·25 g.) from which the *picrate* of (XIII), m. p. 92—93° (orange-red needles from methyl alcohol), was obtained (Found: C, 59·8; H, 5·55. $C_{22}H_{23}O_7N_3$ requires C, 59·9; H, 5·2%).

1 : 4-*Diethyl*-5-*methylnaphthalene* (XV) *and* β-(2 : 5-*Diethylbenzoyl*)*propionic Acid*.—*p*-Diethylbenzene (45·4 g.), condensed in methylene chloride (150 c.c.) with succinic anhydride (43·5 g.) and aluminium chloride (90 g.), gave, after two crystallisations from ligroin, the required *acid* (43 g.; m. p. 67—70°), sufficiently pure for further work. Crystallised from light petroleum it was obtained as rosettes of needles, m. p. 73—74° (Found: C, 71·7; H, 7·95. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

γ-(2 : 5-*Diethylphenyl*)*butyric Acid*.—This was obtained as an oil (32·5 g.), b. p. 208—210°/6—7 mm., when the keto-acid (43 g.) was reduced under Clemmensen conditions. Its p-*nitrobenzylthiuronium* salt (felted needles from dilute alcohol) had m. p. 129° (Found: C, 61·4; H, 6·7. $C_{22}H_{29}O_4N_3S$ requires C, 61·25; H, 6·7%).

5 : 8-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*oxonaphthalene*.—The preceding acid (30 g.) was treated with thionyl chloride (40 c.c.), giving the acid chloride (25 g.), b. p. 167—168°/5—6 mm. This was added to aluminium chloride (30 g.), in methylene chloride (150 c.c.), and set aside overnight. The *tetralone* (17 g.), isolated in the usual way, consisted of an oil, b. p. 164°/5 mm. (Found: C, 83·2; H, 8·9. $C_{14}H_{18}O$ requires C, 83·2; H, 8·9%).

5 : 8-*Diethyl*-1 : 2-*dihydro*-4-*methylnaphthalene*.—The tetralone (7 g.), treated with methylmagnesium iodide, from magnesium (5·1 g.), gave the *dihydro*-compound as an oil (5·8 g.), b. p. 131—135°/7 mm. (Found: C, 90·0; H, 10·2. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%).

5 : 8-*Diethyl*-1 : 2 : 3 : 4-*tetrahydro*-1-*methylnaphthalene* (XIV; R = Me) was obtained from the preceding compound by reduction over Adams's catalyst in acetic acid. It distilled at 126—129°/10 mm. (Found: C, 89·1; H, 10·9. $C_{15}H_{22}$ requires C, 89·1; H, 10·9%).

1 : 4-*Diethyl*-5-*methylnaphthalene* (XV).—The tetrahydro-compound (1 g.), dehydrogenated with either palladised charcoal or selenium, afforded 1 : 4-*diethyl*-5-*methylnaphthalene* (XV) (0·7—0·8 g.), b. p. 129—132°/10 mm. (Found: C, 90·8; H, 9·2. $C_{15}H_{18}$ requires C, 90·9; H, 9·1%). Its *picrate* (orange-red needles from methyl alcohol) had m. p. 105—106° (Found: C, 59·8; H, 4·7. $C_{21}H_{25}O_7N_3$ requires C, 59·0; H, 4·9%).

4 : 5 : 8-*Triethyl*-1 : 2-*dihydronaphthalene*.—5 : 8-Diethyl-1 : 2 : 3 : 4-tetrahydro-1-oxo-

naphthalene (9·3 g.), reacting with ethylmagnesium iodide, from magnesium (6·7 g.), gave the required *dihydro*-compound (8·1 g.) as an oil, b. p. 143—145°/11 mm. (Found: C, 89·1; H, 10·1. $C_{18}H_{22}$ requires C, 89·7; H, 10·3%).

1 : 5 : 8-*Triethyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene* (XIV; R = Et) was quantitatively obtained from the preceding compound by reduction over Adams's catalyst, and was collected at 160—164°/5—6 mm. (Found: C, 88·4; H, 11·3. $C_{16}H_{24}$ requires C, 88·9; H, 11·1%).

1 : 4-Diethylnaphthalene (XVI) was obtained (0·76 g.; b. p. 124—127°/5 mm.) when the preceding compound (1 g.) was dehydrogenated with selenium. It was characterised as its picrate, m. p. and mixed m. p. with authentic material, 91—92° (cf. Arnold and Barnes, *J. Amer. Chem. Soc.*, 1944, **66**, 960). Authentic 1 : 4-diethylnaphthalene was prepared by conventional methods from 5 : 8-diethyl-1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene, and further characterised as its *trinitrotoluene* adduct (yellow prisms from methyl alcohol), m. p. 67—69° (Found: C, 61·7; H, 5·2. $C_{21}H_{21}O_6N_3$ requires C, 61·3; H, 5·1%).

5 : 8-*Dimethyl*-1-*naphthol*.—1 : 2 : 3 : 4-Tetrahydro-5 : 8-dimethyl-1-oxonaphthalene (1·3 g.) (Barnett and Sanders, *J.*, 1933, 434) in ether (5 c.c.) was treated with bromine (0·6 c.c.) in ether (10 c.c.). The crude product, after removal of ether, was refluxed for 45 min. with diethylaniline (4 c.c.), and the product was added to sulphuric acid (50%; 25 c.c.) and distilled in steam. The required *naphthol* (0·22 g.), collected from the distillate, crystallised from light petroleum as radiating needles, m. p. 76° (Found: C, 83·7; H, 6·9. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). Its *picrate* (red needles from benzene) had m. p. 179—181° (Found: C, 54·3; H, 3·7. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·7%). Its *styphnate* (brick-red rods from benzene) had m. p. 165—166° (Found: C, 52·2; H, 3·7. $C_{18}H_{15}O_9N_3$ requires C, 51·8; H, 3·6%).

1 : 2 : 3 : 4-*Tetrahydro*-5 : 8-*dimethyl*-1-*naphthol* (I; R = OH, R″ = H, R′ = R‴ = Me).—The corresponding tetralone (Barnett and Sanders, *loc. cit.*) (7·7 g. in ether, 40 c.c.) was slowly added to lithium aluminium hydride (0·84 g. in ether, 50 c.c.), and the mixture then refluxed for 30 min. The *alcohol* (6·7 g.; m. p. 89—91°), isolated in the usual way, crystallised from light petroleum as prisms, m. p. 90—91° (Found: C, 81·7; H, 9·0. $C_{12}H_{16}O$ requires C, 81·8; H, 9·1%).

1-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 8-*dimethylnaphthalene* (I; R = Br, R″ = H, R′ = R‴ = Me).—The above alcohol (6·3 g.) was mixed with constant-boiling hydrobromic acid (19·2 g.) and concentrated sulphuric acid (5·5 g.), set aside overnight, and then heated on the water-bath for 30 min. The cooled mixture was extracted with ether, from which the *bromo*-compound (7·2 g.; m. p. 32—38°) was obtained. It crystallised from light petroleum as prisms, m. p. 60—61° (Found: C, 60·4; H, 6·5. $C_{12}H_{15}Br$ requires C, 60·3; H, 6·3%). It rapidly decomposed on being warmed.

Action of *Selenium* on 1 : 2 : 3 : 4-*Tetrahydro*-5 : 8-*dimethyl*-1-*oxonaphthalene*. 5′ : 5″-*Dimethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (XIX; R = R′ = H, R″ = Me).—The tetralone (4·2 g.) was heated under standard conditions with selenium, and the mixture extracted with benzene. The extract, washed with sodium hydroxide, yielded (*a*) 5 : 8-dimethyl-1-naphthol (0·15 g.), m. p. 76°, characterised as its picrate, m. p. 179—180°, undepressed by authentic material, prepared as above; and (*b*) the *furan* (0·55 g.), m. p. 178°, raised to 181—182° (felted needles), by crystallisation from benzene–light petroleum (Found: C, 88·8; H, 6·2. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%). Light absorption: Maxima, 2620, 2770, (3000), 3200, 3350, 3500 Å; log ε = 4·84, 4·69, (4·11), 4·03, 4·22, 4·12 respectively. Its *picrate* (red needles from benzene) had m. p. 188—189° (Found: C, 63·7; H, 4·4. $C_{22}H_{16}O,C_6H_3O_7N_3$ requires C, 64·0; H, 3·6%). Its *trinitrobenzene* adduct (orange needles from benzene) had m. p. 208° (Found: C, 66·0; H, 3·8. $C_{22}H_{16}O,C_6H_3O_6N_3$ requires C, 66·0; H, 3·7%).

5 : 7-*Dimethyl*-1-*naphthol and* 2-*Bromo*-1 : 2 : 3 : 4-*tetrahydro*-5 : 7-*dimethyl*-1-*oxonaphthalene*.—1 : 2 : 3 : 4-Tetrahydro-5 : 7-dimethyl-1-oxonaphthalene (Heilbron and Wilkinson, *J.*, 1930, 2537) (1 g.) was treated in ether (5 c.c.) with bromine (0·4 c.c.) in ether (10 c.c.), and set aside for 1 hr. After washing with sodium hydrogen sulphite solution and removal of the ether, the required *bromo*-compound (1·6 g.), m. p. 68—70°, was obtained and crystallised from light petroleum as tufts of needles, m. p. 84° (Found: C, 56·9; H, 4·9. $C_{12}H_{13}OBr$ requires C, 56·9; H, 5·1%).

5 : 7-*Dimethyl*-1-*naphthol*.—The above bromo-compound (0·7 g.), dehydrobrominated as described for its isomer, gave the *naphthol* (0·15 g.) which crystallised from light petroleum as needles, m. p. 79—80° (Found: C, 83·5; H, 7·2. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%). Light absorption: Maxima (in *cyclo*hexane), 2300, 2970, (3140), 3280 Å; log ε = 4·48, 3·66, (3·40), and 3·12 respectively. It gave a green ferric reaction. Its *picrate* (brick-red needles from

methyl alcohol) had m. p. 164—165° (Found : C, 53·6; H, 3·7. $C_{18}H_{15}O_8N_3$ requires C, 53·9; H, 3·7%). Its *trinitrotoluene* adduct (yellow needles from methyl alcohol) had m. p. 102—104° (Found : C, 56·9; H, 4·3. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3%).

Action of Selenium on 1 : 2 : 3 : 4-*Tetrahydro*-5 : 7-*dimethyl*-1-*oxonaphthalene and* 5′ : 5″-7′ : 7″-*Tetramethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (XIX; R = H, R′ = R″ = Me).—The tetralone (4 g.), heated with selenium under standard conditions, gave a product which was extracted with aqueous sodium hydroxide. From the extract a *monohydrate* of 5 : 7-dimethyl-1-naphthol (0·5 g.; needles from light petroleum), m. p. 58—59°, was obtained (Found : C, 75·5; H, 7·0. $C_{12}H_{12}O,H_2O$ requires C, 75·8; H, 7·4%). Light absorption : Maxima (in *cyclo*hexane), 2300, 2940, 3140, 3280 Å; log ε = 4·79, 3·89, 3·52, 3·45 respectively.

The non-acidic fraction of the above product yielded the *furan* (0·4 g.), which crystallised from benzene–light petroleum as pale yellow needles, m. p. 201—202° (Found : C, 88·2; H, 6·0. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%). Light absorption : Maxima (in *cyclo*hexane), 2540, 2660, 2760, 2980, 3100, 3280, 3420, 3560 Å; log ε = 4·66, 4·62, 4·65, 4·41, 4·36, 4·36, 4·54, 4·40 respectively. It gave a green colour with cold concentrated sulphuric acid, changing to deep red on warming. Its *picrate* (brick-red needles from benzene) had m. p. 211° (Found : C, 65·4; H, 4·2. $C_{24}H_{20}O,C_6H_3O_7N_3$ requires C, 65·1; H, 4·2%). Its *styphnate* (deep orange needles from benzene) had m. p. 209—210° (Found : C, 63·8; H, 4·2. $C_{24}H_{20}O,C_6H_3O_8N_3$ requires C, 63·3; H, 4·0%).

Action of Selenium on α-Naphthol.—When α-naphthol (10 g.) was heated under standard conditions with selenium it yielded dinaphtho(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)furan (Clemo, Cockburn, and Spence, *loc. cit.*) (1·3 g.), m. p. and mixed m. p. 181—183°. This gave a *styphnate* (brown needles from benzene), m. p. 187—188° (Found : C, 50·7; H, 2·2. $C_{20}H_{12}O,2C_6H_3O_8N_3$ requires C, 50·7; H, 2·4%).

Action of Selenium on 1 : 2 : 3 : 4-*Tetrahydro*-5 : 7 : 8-*trimethyl*-1-*oxonaphthalene* (Cocker, Cross, and McCormick, *loc. cit.*).—Tetralone (5 g.) gave a mixture from which the following were separated : (*a*) 5′ : 5″ : 7′ : 7″ : 8′ : 8″-*hexamethyldinaphtho*(1′ : 2′-2 : 3)(2″ : 1″-4 : 5)*furan* (0·4 g.) (XIX; R = R′ = R″ = Me), m. p. 269—270° (needles from benzene) (Found : C, 88·2; H, 6·9. $C_{26}H_{24}O$ requires C, 88·6; H, 6·8%), which gave a green colour with cold concentrated sulphuric acid, changing to violet on warming. Its *picrate* (deep red prisms; readily dissociated on warming with benzene) had m. p. 228° (Found : C, 65·8; H, 4·7. $C_{26}H_{24}O,C_6H_3O_7N_3$ requires C, 66·1; H, 4·6%). (*b*) The monohydrate of 5 : 7-dimethyl-1-naphthol (m. p. and mixed m. p.) [picrate, m. p. 163°, undepressed by the picrate of authentic 5 : 7-dimethyl-1-naphthol (see above)].

4-*Ethyl*-1 : 2 : 3 : 4-*tetrahydro*-5-*methoxynaphthalene* (IV) *and* 4-*Ethylcoumarin* (XXIII).—*o*-Methoxypropiophenone (152 g.), ethyl bromoacetate (155 g.), and zinc (61 g.) condensed in boiling benzene (200 c.c.) gave a mixed product (222 g.), b. p. 155—163°/7 mm., of hydroxy- and unsaturated esters. A fraction of b. p. 159°/7 mm. was analysed (Found : C, 68·4; H, 7·8. Calc. for $C_{14}H_{20}O_4$: C, 66·7; H, 7·9. Calc. for $C_{14}H_{18}O_3$: C, 71·8; H, 7·7%). The mixture was refluxed for 10 hr. with hydriodic acid (300 c.c.; *d* 1·7) and red phosphorus (200 g.), then diluted with water, and the oily layer was washed with sodium hydrogen sulphite solution. The colourless oil was fractionated, affording (*a*) *o*-hydroxypropiophenone (55 g.), and (*b*) 4-*ethylcoumarin* (48 g.; b. p. 170—185°/15 mm.). The lactone solidified and then crystallised from light petroleum as needles, m. p. 70° (Found : C, 75·8; H, 5·5. $C_{11}H_{10}O_2$ requires C, 75·9; H, 5·7%).

3-o-*Methoxyphenylpent*-2-*enoic acid* (XXIV) (19 g.), obtained from the lactone (33 g.) by hydrolysis with 10% alcoholic potash, followed by methylation with methyl sulphate, crystallised from dilute alcohol as prisms, m. p. 114° (Found : C, 69·3; H, 6·4. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

3-o-*Methoxyphenylpentanoic acid* (XXV).—The preceding acid (10 g.) reduced in ethyl acetate with Adams's catalyst gave the saturated *acid* (10 g.) as rhombs (light petroleum), m. p. 63° (Found : C, 68·6; H, 7·4. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). Its *amide* (needles from benzene) had m. p. 81·5° (Found : C, 69·9; H, 8·1. $C_{12}H_{17}O_2N$ requires C, 69·6; H, 8·2%).

4-o-*Methoxyphenylhexanamide and the Acid* (XXVI; R = NH_2 and OH respectively).—The acid chloride (6 g.) of (XXV) in ether (20 c.c.) was treated at 0° with diazomethane (2·9 g.) in ether (140 c.c.), and the mixture set aside overnight. The oily diazo-ketone (6·1 g.) was treated in dioxan (60 c.c.), at 50°, with a mixture of 20% ammonia (25 c.c.) and 10% aqueous silver nitrate (4 c.c.), and then heated for 2 hr. on the water bath. The dioxan was removed in a vacuum, and the residue was extracted with ether from which the *amide* (XXVI; R = NH_2)

(4·6 g.; needles from benzene) was obtained, having m. p. 89·5° (Found: C, 70·3; H, 8·6. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6%). The *acid* (XXVI; R = OH) (5·9 g.), m. p. 55—56° (prisms from light petroleum), was obtained by hydrolysis of the amide (6·0 g.) for 3 hr. with a solution of potassium hydroxide (5 g.) in water (30 c.c.) (Found: C, 70·8; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%).

4-Ethyl-1 : 2 : 3 : 4-tetrahydro-5-methoxy-1-oxonaphthalene (XXVII).—Polyphosphoric acid was made by heating phosphoric acid (10 g.; *d* 1·75) with phosphoric oxide (6·4 g.) at 165° for 1 hr. The hexanoic acid (0·4 g.) was added with vigorous stirring to the polyphosphoric acid (2·4 g.) at 165° (cf. Birch, Jaeger, and Robinson, *J.*, 1945, 582), and the temperature maintained thereat for 5 min. The mixture, worked up in the usual way, yielded the required *ketone* (0·27 g.) as an oil, b. p. 171°/15 mm. (Found: C, 76·4; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%).

4-Ethyl-1 : 2 : 3 : 4-tetrahydro-5-methoxynaphthalene (IV) was obtained as an oil (0·34 g.), b. p. 139°/15 mm., when the tetralone (0·5 g.) was reduced under Clemmensen conditions (Found: C, 81·9; H, 9·1. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). Dehydrogenation of this compound (0·32 g.) with selenium gave an oil (0·22 g.), b. p. 140—144°/15 mm., which on demethylation afforded α-naphthol (m. p. and mixed m. p.).

Dehydrogenation of *1-Ethyl-1 : 2 : 3 : 4-tetrahydro-8-methoxy-5 : 7-dimethylnaphthalene* (XVII).—The corresponding dihydro-compound (Cocker *et al.*, *J.*, 1950, 1781) was quantitatively reduced over palladised charcoal, giving the tetrahydro-compound (XVII), b. p. 144—151°/20 mm. It was characterised by demethylation and preparation of the *carbanilate*, m. p. 134—135°, of 8-ethyl-5 : 6 : 7 : 8-tetrahydro-2 : 4-dimethyl-1-naphthol (Found: C, 77·7; H, 7·6. $C_{21}H_{25}O_2N$ requires C, 78·0; H, 7·75%). When the methoxy-compound (1·5 g.) was heated with palladised charcoal, 5-ethyl-1 : 3-dimethylnaphthalene (XVIII) (0·94 g.) was obtained, and characterised as its picrate and trinitrotoluene adduct (Cocker, Cross, and McCormick, *loc. cit.*).

Investigation of the By-products produced in the Dehydrogenation of (I; R = Et, R′ = R″ = R‴ = Me) *with Selenium.*—The tetralin (4 g.) was dehydrogenated, in a current of nitrogen, under standard conditions of temperature, time, and quantity of selenium. The reaction was carried out in a long-necked flask (A) (10 c.c.; 17-cm. neck) with side-arm. This was attached to two traps (*B* and *C*), in series, immersed in liquid air; (*C*) was attached to a flask (*D*), similar to (*A*), which was connected to a short water-cooled condenser, leading to a side-arm test-tube (*E*). This test-tube was attached to an absorption train consisting of two lead acetate (1 l.; 10%), one sodium hydroxide (1 l.; 4%), one lead acetate, and two acid permanganate bubblers. Ground-glass joints were used throughout, and the pressure in the system was kept constant by using a mercury manometer attached to (*A*): (*A*) was heated in an electric furnace.

After 4 hr. the furnace was turned off, and the apparatus was allowed to cool slowly, the stream of nitrogen being adjusted from time to time. After about 1 hr. (*D*) was placed in a freezing mixture (−20°), and the liquid-air containers were removed from (*B*) and (*C*). As these traps reached room temperature, hydrogen selenide was evolved and was collected in the lead acetate train. Finally, (*B*) and (*C*) were warmed in a water-bath, the flask (*D*) being cooled in liquid air, a liquid product thus being collected in (*D*). The liquid was carefully distilled from (*D*) into (*E*) which was cooled in liquid air. The product, ethyl hydrogen selenide (1·02 g.; b. p. 53°), was oxidised with 50% nitric acid (15 c.c.), concentrated, and then treated with concentrated hydrochloric acid, thus affording the hydrochloride of ethylseleninic acid, m. p. 108° (Found: C, 13·6; H, 4·1. Calc. for $C_2H_6SeO_2,HCl$: C, 13·5; H, 3·9%).

The permanganate solutions suffered no reduction, as shown by titration with oxalic acid.

The sodium hydroxide solution was titrated with standard acid, and contained no selenium compound.

The undistilled product remaining in the reaction flask (*A*) yielded pure 1 : 2 : 4-trimethylnaphthalene (0·55 g.) (cf. Part I, *loc. cit.*), and a product (2·0 g.) which by spectroscopy was shown to contain 15—25% of unchanged tetralin (I; R = Et, R′ = R″ = R‴ = Me).

The precipitated lead selenide in the lead acetate bubblers weighed 6·0 g., equivalent to about 70% of 4 H atoms.

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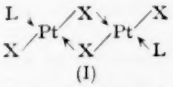
482. *The Nature of the Co-ordinate Link. Part VIII.* Geometrical Isomerism and Simple Reactions of Ethylthio-bridged Complexes of Platinum*(II) *and of Palladium*(II).

By J. Chatt and F. A. Hart.

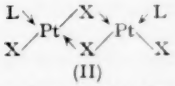
When dichlorobistri-*n*-propylphosphine-μμ′-dichlorodiplatinum (VII) is treated with an excess of ethanethiol, the two bridging chlorine atoms are replaced by SEt groups to yield a mixture of the *trans*- (IV) and *cis*-symmetrical isomers (V) of dichlorobistri-*n*-propylphosphine-μμ′-bisethylthiodiplatinum. Both isomers remain unchanged in benzene solution at room temperature, but the *trans*- changes into the *cis*-isomer in boiling benzene or under the catalytic influence of tri-*n*-propylphosphine. The above dithiol-bridged complexes are not attacked by amines in boiling benzene. The tetrachloro-compound (VII) reacts with the dithio-compounds (IV) and (V) to yield *cis*-SPS-*cis*-symmetrical-dichlorobistri-*n*-propylphosphine-μ-chloro-μ′-ethylthiodiplatinum † (VI). This is attacked in solution by amines as if it existed in equilibrium with a mixture of the above dithio-compounds and the tetrachloro-compound. The tetrachloro-compound has a *trans*-configuration, but in solution it exists in equilibrium with about 2% of its *cis*-isomer. This equilibrium appears to be established by a very slight reversible dissociation of the tetrachloro-compound at the bridge to give the configurationally unstable $PPr^n_3PtCl_2$. The corresponding mono- and bis-ethylthio-bridged palladium complexes also have *cis*-configurations. The surprisingly high stability of the *cis*-isomers relative to the *trans*-isomers when sulphur occupies one or both of the bridging positions is discussed. It is evidence of some strong directing influence in the Pt–S–Pt–S and Pd–S–Pd–S rings. The dipole moments of the above compounds, used to determine their configurations, are listed.

Pfeiffer, in 1923 (Werner and Pfeiffer, "Anorganische Chemie," 5th Edn., pp. **56**, 170) suggested that the few platinous complexes of the type $LPtX_2$ [L = ligand, *e.g.*, CO, PCl_3, $P(OEt)_3$; X = halogen] which were then known would have halogen-bridged structures. He also noted that three isomeric forms are possible. These may be represented by (I), (II), and (III):



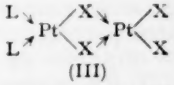
(I)

"*trans*-symmetrical"



(II)

"*cis*-symmetrical"



(III)

"unsymmetrical"

This isomerism is theoretically possible in similar complexes of any bivalent metal whether it be co-ordinated in a plane or tetrahedrally; yet out of the numerous bridged complexes now known, only *trans*-symmetrical forms (I) have been identified (*e.g.*, Mann and Wells, *J.*, 1938, 702; Wells, *Proc. Roy. Soc.*, 1938, *A*, **167**, 169). Of the 4-co-ordinated metals, platinum(II) forms the most robust complexes, hence geometrical isomerism is more probable among its bridged complexes than among those of any other metal. In Part II (Chatt, *J.*, 1951, 652) we briefly reviewed previous work and described the halogen-bridged platinous complexes of tri-*n*-propylphosphine, among which we failed to find geometrical isomerism. There are three possible causes for this failure: (1) The four methods of preparation we used yielded exclusively the *trans*-symmetrical isomer, by which it is implied that some other method might yield exclusively the *cis*-isomer. (2) The terminal X and L groups can interchange positions spontaneously so that an equilibrium mixture of isomers exists in solution. This suggestion has already been made with reference to the analogous palladous series of complexes (Mann, *Ann. Reports*, 1938, **35**, 150; Chatt and

* Part VII, *J.*, 1953, 70.

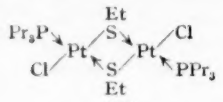
† For this nomenclature, see p. 2365.

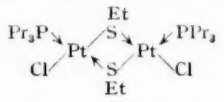
Mann, *J.*, 1939, 1622). (3) In solution the complex is slightly dissociated at the bridge into two fragments, $LPtX_2$, which would be configurationally unstable. They thus yield an equilibrium mixture from which only the stable (usually *trans*-)bridged isomer can be isolated. Dissociation of this type has been suggested to explain reactions in the cadmium and mercury series of complexes (Mann and Purdie, *J.*, 1940, 1230) of the type:

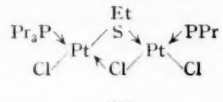
$$(Pr^n_3P)ICdI_2CdI(PPr^n_3) + (Pr^n_3P)IHgI_2HgI(PPr^n_3) \longrightarrow (Pr^n_3P)ICdI_2HgI(PPr^n_3)$$

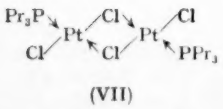
We suspected the third cause to be responsible for our failure to isolate geometrically isomeric forms of the halogen-bridged $(PPr^n_3)_2Pt_2Cl_4$. In the palladous series of complexes, the ethylthio-group is known to be much more strongly bridging than the halogen atom (Chatt and Mann, *J.*, 1938, 1949); we have, therefore, prepared the thio-bridged $(PPr^n_3)_2Pt_2(SEt)_2Cl_2$. The bridge in this compound has proved sufficiently stable to allow us to isolate two geometric isomers (IV) and (V), both of which are stable at room temperature. Surprisingly the *cis*-isomer (V) is the thermodynamically stable isomer in benzene solution. In consequence of this, we have examined the configuration of the bridged monothio-complex $(PPr^n_3)_2Pt_2(SEt)Cl_3$ and the bridged palladium complexes $(PPr^n_3)_2Pd_2(SEt)_2Cl_2$ and $(PPr^n_3)_2Pd_2(SEt)Cl_3$. All are *cis*-isomers of type (II), but the palladous complexes isomerise in benzene at 25° to yield equilibria in which the *cis*-isomers predominate.

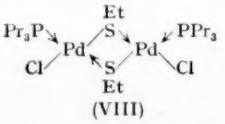
The compounds which form the subject of this paper have been allocated structures as follows; all except (VII) are new and some of their physical properties are listed in Tables 1 and 2, p. 2367.

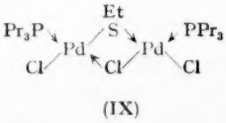

(IV)


(V)


(VI)


(VII)

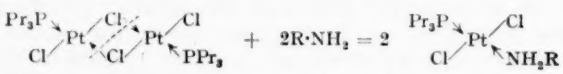

(VIII)


(IX)

When ethanethiol in excess (4—8 mols.) was added to a solution of the tetrachloro-compound (VII), the colour changed immediately from orange to yellow. Evaporation now yielded a sticky mixture containing the monothio- (VI) and the dithio-compounds (IV) and (V). More prolonged action of ethanethiol (6 hr.) yielded only the dithio-compounds; no evidence of further substitution was obtained even after 3 days. The monothio-compound (VI) is best prepared by boiling the dithio-compounds, either (IV) or (V), with their equivalent of the tetrachloro-compound (VII) in benzene but may also be obtained by reaction of one molecule of ethanethiol with (VII).

Structure and Configuration of the Bridged Ethylthioplatinous Complexes.—The methods of synthesis, the analysis, and molecular weights indicate the formula $(PPr^n_3)_2Pt_2(SEt)_2Cl_2$ for the dithio-compounds (IV) and (V), and $(PPr^n_3)_2Pt_2(SEt)Cl_3$ for the monothio-compound (VI). These substances are non-electrolytes in nitrobenzene solution; thus they can only be formulated by bridged as opposed to ionic, *i.e.*, salt, structures.

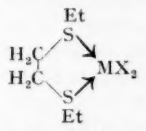
Halogen-bridged platinous complexes are split at the bridge immediately on being mixed with amines in cold solvents (Part II, *loc. cit.*). Both *p*-toluidine and dipyridyl are



without action on the dithio-compounds either in cold or boiling solvents; hence the SEt groups occupy the bridging positions and stabilise the bridge as they do in the analogous palladous series of complexes (Chatt and Mann, *J.*, 1938, 1949). The monoethylthio-compound (VI) reacts only slowly with amines in boiling benzene; its reaction with 2 : 2′-

dipyridyl in nitrobenzene at room temperature requires some six days to go to completion. The bridge is thus intermediate in stability between the very reactive halogen bridge of the tetrachloro-compound (VII) and the stable dithiol bridges. This is consistent with a bridge containing both SEt and Cl as shown in formula (VI). The relative positions of the two tri-*n*-propylphosphine molecules and the chlorine atoms were determined by measuring the dipole moments of the compounds. *trans*-Symmetrical forms, type (I), will have zero dipole moments; *cis*-symmetrical forms, type (II), should have moments approximating to that of *cis*-$(PPr^n_3)_2PtCl_2$ which Jensen (*Z. anorg. Chem.*, **1936**, **229**, 250) found to be 11·5 D; unsymmetrical forms, type (III), should have moments approaching twice this value, say 20 D. The moments listed in Table 1 (p. 2367) show that the dithio-compound of m. p. 156·5—157·5° is *trans*-symmetrical dichlorobistri-*n*-propylphosphine-$\mu\mu'$-bisethylthiodiplatinum (IV), and the compound of m. p. 125·5—127° is its *cis*-isomer (V). The monothio-derivative (Table 2, p. 2367) is also a *cis*-symmetrical isomer and its appreciably higher dipole moment indicates that the most electropositive donors, phosphorus and sulphur, must be arranged along one edge of the molecule as formulated in (VI). No rules of nomenclature have yet been proposed to distinguish this structure from the structure (XIV) (p. 2368). We * have therefore adopted the proposal to prefix the name with *cis*-PSP- to indicate that these three atoms all lie on the same side of the planar molecule. The monothio-compound (VI) is thus *cis*-PSP-*cis*-symmetrical-dichlorobistri-*n*-propylphosphine-μ-chloro-μ'-ethylthiodiplatinum. The unknown compound of structure (XIV) would have the same name except that the prefix would be *cis*-PClP.

Besides the isomerism discussed above, it is possible for each of the dithio-compounds (IV) and (V) to exist in two geometrically isomeric forms because the three bonds from the sulphur atom are not planar, and the ethyl groups may be in *cis*- or *trans*-relation to each other about the Pt–S–Pt–S ring.† Such isomerism was sought by Bennett, Mosses, and Statham (*J.*, 1930, 1668) in complexes of type (X) (MX_2 = $PdCl_2$ or HgI_2) but was not observed, presumably because the sulphur atoms pass easily through the plane of the three attached groups. It would be possible to determine the relative configuration of the ethyl groups in the *trans*-dithio-compound (IV) if we could measure its dipole moment accurately. If the ethyl groups are in *trans*-positions the molecule would be centro-symmetrical and have zero moment; if they are in *cis*-positions the moment would be of the order 1 D.



M = Bivalent metal
(X)

Unfortunately, it is not possible to determine the dipole moments of complex compounds which have small moments from measurements made on solutions of the compound. This arises because the atom polarisation in metallic complexes is large and cannot be estimated with any certainty (*e.g.*, see Part VII, *loc. cit.*). Jensen (*Z. anorg. Chem.*, 1936, **229**, 225) found that an atom polarisation of about 20% of the electron polarisation was generally necessary so that a number of completely symmetrical *trans*-complexes of the type $(MR_3)_2PtCl_2$ (M = P or As) should have zero moment. We find that an allowance for the atom polarisation of 15% of the electron polarisation is necessary if the *trans*-dithio-compound (IV) is to have zero moment. If the moment were greater than zero then the allowance must be less than 15%, which is rather low for compounds of this type. It is very probable, therefore, that the moment really is zero and the ethyl groups are in *trans*-relation about the Pt–S–Pt–S ring. Uncertainty regarding the atom polarisation does not affect the values of the order 10 D recorded for other compounds in this series, because the contributions of the atom polarisations to the total polarisations of these highly dipolar molecules is negligible.

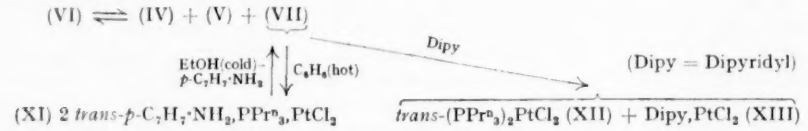
Reactions of the Bridged Ethylthio-compounds (IV), (V), *and* (VI).—The *cis*-dithio-compound (V) is the more stable and it is recovered unchanged after 21 hr. in boiling benzene. The *trans*-isomer (IV) is stable in cold benzene but is slowly converted into the

* We are indebted to the Editor for suggesting this logical extension of existing nomenclature.

† We have some evidence that the S–Pt–S–Pt ring is "aromatic" in character. The S–C bonds and the ring could thus be coplanar.

cis-isomer in boiling benzene. This isomerisation is not appreciably catalysed by the presence of 2 equivalents of *p*-toluidine or 2 : 2′-dipyridyl but occurs rapidly even in cold benzene on addition of a trace of tri-*n*-propylphosphine (cf. Chatt and Wilkins, *J.*, 1951, 3061). The *cis*-isomer is not changed even in presence of a trace of PPr^n_3, so the equilibrium between the two geometric isomers (IV) and (V) lies completely, or almost completely, on the *cis*-side.

The monoethylthio-compound (VI) reacts with amines as if there existed sluggishly established equilibria as follows:



The evidence is:

(*a*) The dithio-compounds (IV) and (V) react with the tetrachloro-compound (VII) in boiling benzene to yield the monothio-compound (VI) quantitatively in less than an hour. At room temperature the reactions require about 3 days, even when the tetrachloro-compound is present in excess.

(*b*) One mol. of 2 : 2′-dipyridyl in a boiling benzene solution of the monothio-compound (VI) reacts slowly (36 hr.) to yield a mixture of (XII), (XIII), the dithio-compounds (IV) and (V), and the excess of dipyridyl. The tetrachloro-compound (VII) is known to react with dipyridyl to yield the salt $[dipy,PPr^n_3,PtCl]^+[PPr^n_3PtCl_3]^-$ (Chatt, *J.*, 1951, 652) which decomposes in boiling solvents to yield (XII) and (XIII), a reaction which is not reversible. By repeating the reaction in nitrobenzene at room temperature in a conductivity cell, the formation of a salt was observed. The non-conducting solution of the monothio-compound (VI) became conducting on addition of dipyridyl, and the conductivity continued to rise for 6 days after the addition.

(*c*) The monothio-compound (VI) reacts sluggishly with 2 mols. of *p*-toluidine in boiling benzene. After 23 hours' reaction, we isolated a trace of (VI), (XI), and the dithio-compound (V) with a small proportion of the *trans*-isomer (IV). The reverse reaction was demonstrated by dissolving 2 equivalents of (XI) in a saturated solution of the dithio-compound (IV) in ethanol at 35—40°. After 3 days at room temperature, a small quantity of the rather sparingly soluble monothio-compound (VI) had separated; (IV), (V), (VI), and (XI) were isolated from the alcoholic solution. Spectrophotometrically it was shown that in 10^{-5}M-ethanol solution the equilibrium lies entirely on the side of the free monothio-compound (VI) and *p*-toluidine. It is to be noted that in the reaction with amines, twice the quantity of amine necessary for the reactions which occurred was used, so that if a simple bridge-splitting reaction (p. 2364) had been possible there was sufficient amine to allow it to happen.

The chemistry of the bridged ethylthio-compounds (IV), (V), and (VI) is obviously closely analogous to that of the corresponding tri-*n*-butylphosphine *palladous* bridged ethylthio-compounds described by Chatt and Mann (*J.*, 1938, 1949). However, the above reactions of the platinous complexes, even when carried out in boiling solvents, are much slower than in the palladous series where even the slowest of the analogous reactions is complete in about an hour at room temperature.

Comparison of the Physical Properties of Simple and Bridged Geometrical Isomers in the Platinous Series of Complexes.—The dithio-compounds (IV) and (V) provide the first examples of bridged *trans*- and *cis*-complexes. Their more obvious physical properties are in marked contrast with those of their simple analogues, *trans*- and *cis*-$(PPr^n_3)_2PtCl_2$. The last two isomers differ markedly in melting point, colour, and solubility, whereas (IV) and (V) show a close resemblance to each other. The slight differences which do occur are in the opposite sense to the greater differences between the properties of members of the simple series (see Table 1).

Configuration of Ethylthio-bridged Palladous Complexes.—In view of the surprisingly high stability of the ethylthio-bridged platinous complexes (V) and (VI) of *cis*-configuration, it

was of interest to determine the configurations of the ethylthio-bridged palladous complexes $(PPr^n_3)_2Pd_2(SEt)_2Cl_2$ and $(PPr^n_3)_2Pd_2(SEt)Cl_3$. A comparison of *X*-ray powder photographs, for which we are indebted to Dr. P. G. Owston, shows that the dithiopalladous

TABLE 1. *A comparison of trans- and cis-*$(PPr^n_3)_2PtCl_2$ *with trans- and cis-*symmetrical-$(PPr^n_3)ClPt(SEt)_2PtCl(PPr^n_3)$.

	$(PPr^n_3)_2Pt_2(SEt)_2Cl_2$		$(PPr^n_3)_2PtCl_2$	
Property	*trans* (IV)	*cis* (V)	*trans*	*cis*
M. p.	156·5—157·5°	125·5—127°	85—86°	150·5—152°
Colour	Very pale yellow	Pale yellow	Pale yellow	Colourless
Solubility in organic solvents	Moderately soluble	Moderately soluble	Very soluble	Moderately soluble
	< (V)	> (IV)	—	—
Dipole moment	~0	10·3D	~0	11·5D
Approx. equil. % of isomers	<1	>99	97	3

complex is isomorphous with the *cis*-dithioplatinous complex (V) and has the same unit-cell size, so must have a *cis*-configuration (VIII). This is confirmed by the dipole moments recorded in Tables 1 and 2. The *trans*-platinous isomer (IV) gives a different photograph. The monothio-platinous and -palladous complexes are also isomorphous and have identical unit-cell size, so these also have the same configurations (VI) and (IX).

TABLE 2. *Melting points, colours, and dipole moments of* (VI), (VIII), *and* (IX).

$(PPr^n_3)_2Pt_2(SEt)Cl_3$ (VI)	$(PPr^n_3)_2Pd_2(SEt)_2Cl_2$ (VIII)	$(PPr^n_3)_2Pd_2(SEt)Cl_3$ (IX)
220—221·5°	136·5—137°	224—224·5°
Pale yellow	Yellow	Yellow
13·0 D	10·7 D	8·3 D *

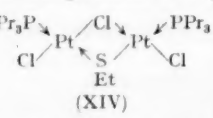
* This is obviously a solution of an equilibrium mixture containing about 35% of related *trans*-complexes.

The dielectric constants of the benzene solutions of (VI) and (IX) at 25° were steady, but that of (VIII) fell slowly, reaching equilibrium after about 25 hr. If we assume, as is most probable, that this drop is caused by isomerisation to a mixture of palladium analogues of the dithio-compounds (IV) and (V), then the equilibrium mixture contains about 90% of the *cis*-isomer. This is the greatest amount of a palladous complex of *cis*-configuration ever recorded in a labile system (cf. Chatt and Wilkins, *J.*, 1953, 70). (IX) has rather poor solubility in pure benzene and slight warming was necessary to get it into solution. The rather low moment found corresponds to a solution containing about 65% of *cis*-isomers in equilibrium with *trans*-isomers. Since the dielectric constant of this solution did not vary with time, isomerisation must have been complete in the time necessary to prepare the solution for measurement. This isomerisation may also be accompanied by a small amount of disproportionation, yielding small quantities of (VIII) and the palladium analogue of (VII) (see Chatt and Mann, *J.*, 1938, 1949).

That the moment of the dithiopalladium compound (VIII) is slightly greater than that of its platinum analogue (V), if significant, is interesting, because it agrees with the expectation that double bonding between ligand and metal is greater in platinous than in palladous complexes. It is also interesting that, when the equilibria between *cis*- and *trans*-platinous complexes are compared with those between the corresponding palladous complexes, the equilibria lie much farther to the *trans*-side in the palladous series (Chatt and Wilkins, *loc. cit.*). The above bridged complexes show the same relation. We regard this as evidence that directing forces (*e.g.*, the *trans*-effect) are considerably weaker in palladous than in platinous complexes.

That the *cis*-configuration of the thio-bridged platinous complexes is preferred is evidence of some strong directing influence in the $\overline{Pt{-}S{-}Pt{-}S}$ ring. This influence is obviously much weaker when the sulphur is replaced by chlorine. The greater covalent character and polarisability of the sulphur ring system, and the non-planar arrangement of the bonds from the sulphur atoms (which confers some asymmetry on its electronic structure), are possible factors responsible for directing the PPr_3 group into *cis*-positions. Whatever may be the cause of the stability of the sulphur-bridged *cis*-isomers, it is of fundamental importance to any theory of substitution in complex compounds and in

establishing the nature of the co-ordinate link itself. That the configuration (VI) should be more stable than (XIV) is a simple manifestation of the *trans*-effect. We have shown in the previous four parts of this series that when a simple platinous complex contains two groups of fairly high *trans*-influence then the *cis*-isomers have a greater bond energy than the *trans*. Both sulphur and phosphorus have a fairly high *trans*-influence. In (XIV) these atoms are in *trans*-positions about both platinum atoms whereas in (VI) they are in *cis*-positions. Thus (VI) should have the greater bond energy and in absence of any unusual entropy difference between (VI) and (XIV) should be the stable isomer. The monothio-platinum compound (VI) is a most unusual molecule in having all the electropositive atoms, P and S, along one edge and the three electronegative chlorine atoms along the opposite edge, giving us the very high dipole moment of 13·0 D, which demonstrates further the unexpectedly powerful directing influences in platinous complexes.



(XIV)

The Nature of the Equilibria in Solutions of Halogen-bridged Platinous and Palladous Complexes.—Mann and his co-workers (Mann, *Ann. Reports*, 1938, **35**, 148; Chatt and Mann, *J.*, 1939, 1622) reached the conclusion that halogen-bridged palladous complexes of trialkyl-phosphines and -arsines exist in solution as equilibrium mixtures of the symmetrical forms of types (I) and (II). There was no evidence for the existence of the unsymmetrical isomer of type (III). All attempts to prepare a compound of the last type by using chelating diarsines and disulphides as ligands had failed. Now we know that such a complex would have a moment of the order of 20 D, and a large amount of electrical energy would be stored in the molecule. It therefore seems very unlikely that any except the minutest quantity of an isomer of type (III) could exist in equilibrium with its symmetrical isomers even if it is capable of existence. Thus we need consider only types (I) and (II) as being present in the equilibrium. The only evidence that any of the *cis*-symmetrical type (II) exists in a solution of the *trans*-symmetrical isomer type (I) is provided by the small but definite apparent dipole moments of the *trans*-bridged complexes in benzene solution. These are too high to be accounted for by assuming a high but reasonable value for the atom polarisation. Mann and Purdie (*J.*, 1936, 873) recorded the dipole moment of $(PBu^n_3)_2Pd_2Cl_4$ as 2·34 D, but made no allowance for atom polarisation. Experience gained since 1936 indicates that 20% of the electron polarisation is a fair approximation to the atom polarisation (Jensen, *loc. cit.*); the moment recalculated on this basis is 1·9 D. We find the moment of $(PPr^n_3)_2Pt_2Cl_4$ to be 1·6 D. Thus in both the palladous and the platinous series of halogen-bridged complexes, we have small moments of the same order of magnitude. These can be accounted for by supposing (*a*) that in each case we have the *cis*-symmetrical isomer in equilibrium with its *trans*-isomer, (*b*) that partial reversible dissociation occurs, giving two highly dipolar fragments, thus: $(PPr^n_3)_2Pt_2Cl_4 \rightleftharpoons 2(PPr^n_3)PtCl_2$, or (*c*) that the compounds have atom polarisations of the order of 50% of the electron polarisations. If dissociation (*b*) were responsible for the observed moments then the observed total polarisation should vary with dilution of the solution. We find that it does not. An atom polarisation as high as 50% of the electron polarisation, as required by (*c*), is very improbable. It lies around 20% in all previously measured symmetrical platinous complexes and cannot be greater than 15% in the sulphur-bridged complex (IV). Supposition (*a*) provides the most probable explanation and has already been made with reference to the palladous complexes (Mann, *loc. cit.*, 1938; Chatt and Mann, *J.*, 1939, 1622). If we assume that the *cis*-symmetrical halogen-bridged complexes have moments of the same order as that found for the *cis*-dithio-compound (V), *viz.*, 10 D, then the equilibrium mixture need contain only about 2% of *cis*-isomer to account for the observed small moments.

The nature of the reactions by which the equilibria are established in the platinous series is also evident. The isomerisation could occur either by interchange of positions by the terminal singly bound ligands or through a very slight dissociation at the bridge into two configurationally unstable fragments, $PPr^n_3,PtCl_2$. If the former explanation were correct, then replacement of the bridging halogen atoms by sulphur atoms should increase the rate of isomerisation. This would be expected because all the terminal ligands are in

trans-positions relative to the bridging groups and sulphur has a greater *trans*-labilising effect than chlorine. If the second explanation were correct the rate of isomerisation should be decreased because the stronger sulphur bridge would be less dissociated than the halogen bridge. Since the latter is what we have found, the isomerisation of the halogen-bridged platinous complexes must occur through dissociation of the bridge. The dissociation is too small to be detected by molecular-weight determinations made in the usual manner (with a micro Swietoslawski apparatus and Beckmann thermometer) or to make a detectable contribution to the apparent dipole moment of the tetrachloro-compound (VII) at the concentrations we used.

The same explanation is probably correct in the case of the palladous bridged complexes because isomerisation of the dithiopalladium compound (VIII) is measurably slow, a most unusual phenomenon amongst palladous complexes containing only monodentate ligands. Such dissociation would account also for the ease with which the bridging halogen atoms can be replaced by many acid radicals, including even the bivalent oxalate radical (Chatt, Mann, and Wells, *J.*, **1938**, 2086).

Experimental

Microanalyses are by Mr. W. Brown of these laboratories.

Reaction of Dichlorobistri-n-*propylphosphine*-μμ′-*dichlorodiplatinum* (VII) *with Ethanethiol.*—Ethanethiol (1·45 g.) was added to (VII) (5 g., 0·25 mol.) in acetone (150 c.c.). The solution which immediately changed colour was kept for 6 hr. and then evaporated under reduced pressure. The residual solid was recrystallised from ethanol, giving 4·48 g. of mixed isomers (IV) and (V). These were separated by allowing their solution in hot ethanol (200 c.c.) to cool slowly, giving needles (1·7 g.), m. p. 150—153·5°. The mother-liquor from these was evaporated to 70 c.c. and then on slow cooling yielded thick plate-like tablets (1·6 g.), m. p. 121—125·5°. The needles, recrystallised three times from acetone, yielded pure trans-*symmetrical-dichloro-bistri*-n-*propylphosphine*-μμ′-*bisethylthiodiplatinum* (IV) (0·96 g.), m. p. 156·5—157·5° (Found: C, 29·2; H, 5·8; S, 6·9%; *M*, ebullioscopically in 1·87% benzene solution, 896; in 2·81% solution, 923. $C_{22}H_{52}Cl_2S_2P_2Pt_2$ requires C, 29·2; H, 5·8; S, 7·1%; *M*, 904). The tablets, recrystallised four times from ethanol, yielded the pure cis-*symmetrical-isomer* (V) (0·86 g.), m. p. 125·5—127° (Found: C, 29·3; H, 5·82; S, 7·1%; *M*, ebullioscopically in 1·82% benzene solution, 919; in 3·13% solution, 884). Repetition of this reaction with only 0·125 mol. of (VII) and keeping the mixture for 3 days gave identical products. Repetition, except that the products were worked up immediately after mixing, yielded a gum from which we isolated cis-*PSP*-cis-*symmetrical-dichlorobistri*-n-*propylphosphine*-μ-*chloro*-μ′-*ethylthiodiplatinum* (VI) (1·8 g.), m. p. 220—221·5° (Found: C, 27·4; H, 5·55; S, 3·5%; *M*, ebullioscopically in 1·41% acetone solution, 911; in 1·81% solution, 914. $C_{20}H_{47}Cl_3SP_2Pt_2$ requires C, 27·3; H, 5·6; S, 3·65%; *M*, 878).

The monothio-compound (VI) was prepared quantitatively, and pure without recrystallisation, by boiling a solution of equivalent quantities of (VII) and the mixed isomers (IV) and (V) in benzene (1 g. of solid in 10 c.c.) for 1 hr.

Reaction of (VII) *with Pure* (IV) *and with Pure* (V) *in Cold Benzene.*—Solutions of (IV) (0·1 g.) and (V) (0·1 g.) were made up separately in benzene (1 c.c. each). To those were added (VII) (0·075 g., 0·8 mol.) in benzene (1 c.c.). Slow colour change was apparent within 10 min. of mixing; fine needles started to be deposited from (IV) after 1 hr., and heavier, thicker needles from (V) after 1·75 hr. Deposition continued from both solutions for about 3 days. The product from both reactions had m. p. 220—222° alone and mixed with authentic (VI).

Preparation of Dichlorobistri-n-*propylphosphine*-μ-*chloro*-μ′-*ethylthiopalladium* (IX) and *Dichlorobistri*-n-*propylphosphine*-μμ′-*bisethylthiodipalladium* (VIII).—Ethanethiol (1·28 g., 3 mols.) was added slowly to a solution of the palladium analogue of (VII) (5 g.) in acetone (200 c.c.). Crystals started to separate immediately and after 70 hr. were filtered off. These were pure *monothio*-derivative (IX) (2·9 g.), m. p. 224° (Found: C, 34·5; H, 7·0; S, 4·45. $C_{20}H_{47}Cl_3SP_2Pd_2$ requires C, 34·3; H, 6·8; S, 4·6%). The mother-liquor was evaporated, to yield a solid (1·71 g.) which was extracted with cold benzene leaving a slight residue of (IX). The *dithio*-derivative (VIII) (1 g.), m. p. 137°, was recovered from the benzene solution and was pure after three recrystallisations from methanol (Found: C, 36·5; H, 7·55; S, 8·9%; *M*, ebullioscopically in 1·48% benzene solution, 724; in 2·14% solution, 718. $C_{22}H_{52}Cl_2S_2P_2Pd_2$ requires C, 36·35; H, 7·2; S, 8·8%; *M*, 727).

Conductivity.—All the platinum complexes were tested for electrolytic properties by

measuring the conductivity of a solution of the complex (0·25 g.) in nitrobenzene (10 c.c.), using the cell and apparatus described in *J.*, 1951, 652. The conductivities observed were of the order 0—0·1 μmho, whereas a uni-univalent electrolyte should give a conductivity of about 800 μmhos.

Dipole Moments.—Dielectric constants (ε) were measured with a heterodyne beat capacity meter based on that of Hill and Sutton (see Everard and Sutton, *J.*, 1949, 2313) and a rhodium-plated cell of the same dimensions and design as that of Jenkins and Sutton (*J.*, 1935, 609). The refractive indices (n) were determined with a Pulfrich refractometer and specific volumes (v) with the usual U-shaped pyknometer. Small dipole moments were evaluated by the method of Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, **46**, 417). It was assumed, however, that the atom polarisation (${}_AP$) is equal to 20% of the electron polarisation (${}_EP$) and that ${}_EP$ is equal to the molar refractivity for the red hydrogen line (λ 6562·8 Å). These assumptions were made on good grounds by Jensen (*loc. cit.*) for a series of platinous complexes, and our moments are thus comparable with his. Large moments, of the order of 10 D, were calculated with sufficient accuracy by using Jensen's approximate formula (*Acta Chem. Scand.*, 1949, **3**, 479). The measurements are recorded in Table 3. w is the weight fraction of solute, $\Delta\varepsilon = \varepsilon_s - \varepsilon_B$ where ε_s = dielectric constant of solution, ε_B = dielectric constant of benzene, and similarly for Δn and Δv. All measurements were made in benzene solution at 25°. The value $\varepsilon_B = 2{\cdot}2727$ was used to calibrate the capacity meter (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 683).

TABLE 3.

10^3w	$10^3\Delta\varepsilon$	$10^3\Delta n$	$-10^3\Delta v$	${}_TP$	${}_EP$	${}_OP$	μ
trans-$(PPr_3)_2Pt_2(SEt)_4Cl_2$ (IV)							
11·38	5·438	—	—	—	—	—	—
17·92	8·168	—	1·0	—	—	—	—
43·90	—	2·798	—	—	—	—	—
33·44	—	2·012	—	—	—	—	—
19·75	—	1·125	—	236·8	205·6	−10	~0
				If ${}_AP$ = 15% of ${}_EP$, then μ is exactly 0.			
cis-$(PPr_3)_2Pt_2(SEt)_2Cl_2$ (V)							
20·90	281·7	—	1·20	—	—	2150 *	—
9·477	124·8	—	—	—	—	2180 *	—
3·935	51·28	—	—	—	—	2190 *	10·3 *
66·695	—	4·148	—	—	—	—	—
48·68	—	3·013	—	2426	199	2187	10·3
$(PPr_3)_2Pt_2Cl_4$ (VII)							
34·83	25·30	—	—	—	—	—	—
21·54	15·60	—	—	—	—	—	—
42·52	31·50	—	—	—	—	—	—
37·58	27·62	—	—	—	—	—	—
66·89	—	3·430	—	—	—	—	—
52·80	—	2·659	—	—	—	—	—
6·42	—	—	0·41	—	—	—	—
10·65	—	—	0·68	246·3	163·6	50·0	1·6
$(PPr_3)_2Pt_2(SEt)Cl_3$ (VI)							
2·87	60·96	—	—	—	—	3460 *	13·0 *
0·8407	17·44	—	—	—	—	3410 *	
$(PPr_3)_2Pd_2(SEt)_2Cl_2$ (VIII)							
7·441	129·1	—	—	—	—	2300 *	10·7 *
3·435	60·4	—	—	—	—	2370 *	
$(PPr_3)_2Pd_2(SEt)Cl_3$ (IX)							
0·7175	7·662	—	—	—	—	1400 *	8·3 *
0·638	7·045	—	—	—	—	1450 *	

* Calculated by Jensen's approximate formula. The benzene used had a d^{25} 0·8734. To convert the weight fractions into molar concentrations for substitution in Jensen's formula we assumed that the solution had the same density as the benzene. The error thus introduced is 0·02 D in moments of 10 D measured under the above conditions. The above moments are accurate to ±0·1 D.

Reactions of the cis-*Dithio-* (V), trans-*Dithio-* (IV), *and Monothio-* (VI) *compounds with Amines.*—Products were identified by mixed m. p. with authentic specimens.

(*a*) (V) *with* p-*toluidine.* *p*-Toluidine (0·241 g., 2 mols.) was refluxed with (V) (1 g.) in benzene (25 c.c.) for 16 hr., and the solution was then taken to dryness under reduced pressure. The residue (0·92 g.) washed with ethanol was almost pure (V), m. p. 122·5—123·5°. *p*-Toluidine (0·12 g.) was recovered from the alcoholic washings.

(*b*) (V) *with* 2 : 2′-*dipyridyl*. Experiment (*a*) was repeated, but with dipyridyl (0·173 g., 1 mol.) instead of *p*-toluidine, with similar results.

(*c*) (IV) *with* p-*toluidine*. The experiment was carried out exactly as (*a*). Mixed (IV) and (V), m. p. 138—143° (0·90 g.), were recovered and separated in almost pure condition by fractional crystallisation from alcohol, giving (IV) (0·22 g.), m. p. 154°, and (V) (0·08 g.), m. p. 127°. *p*-Toluidine (0·13 g.) was recovered.

(*d*) (IV) *with* 2 : 2′-*dipyridyl*. The experiment was carried out as (*b*), except that the reaction time was 22 hr. Mixed (IV) and (V) (0·98 g.), m. p. 133—137°, were recovered and separated as in (*c*). Dipyridyl (0·1 g.) was recovered.

(*e*) (VI) *with* p-*toluidine*. *p*-Toluidine (0·487 g., 2 mols.) was added to (VI) (2 g.) in boiling benzene (135 c.c.), and the whole refluxed for 23 hr. and then evaporated to dryness. The residue was extracted with ether and crude *trans*-*p*-toluidinetri-*n*-propylphosphinedichloroplatinum (XI) (0·85 g.) obtained by evaporation of the ethereal extract. Thrice recrystallised from methanol it had m. p. 111°. The residue (1·11 g.) from the ethereal extraction was mainly (V). It was extracted with hot alcohol, leaving 0·04 g. of unchanged (VI), and on cooling the alcohol deposited a yellow solid, m. p. 125—135°. The latter was fractionally recrystallised, to yield pure specimens of (IV) and (V).

(*f*) (VI) *with* 2 : 2′-*dipyridyl*. 2 : 2′-Dipyridyl (0·177 g., 1 mol.) was boiled with (VI) (1 g.) in hot benzene (65 c.c.) for 34 hr. Fine insoluble red and yellow needles of 2 : 2′-dipyridyldichloroplatinum (XIII) separated during the reaction and were filtered off (Found : C, 28·7; H, 1·9. Calc. for $C_{10}H_8Cl_2Pt$: C, 28·4; H, 1·9%). The benzene solution worked up as (*e*) yielded a mixture of (IV) and (V) (0·4 g.), m. p. 125—135°, and *trans*-$(PPr^n_3)_2PtCl_2$ (XII) (0·49 g. crude). Thrice recrystallised from methanol the last had m. p. 85°.

(*g*) *Reversal of reaction* (*e*). The compound (IV) (0·25 g.) and *trans*-*p*-$C_7H_7{\cdot}NH_2,PPr^n_3,PtCl_2$ (XI) (0·295 g., 2 mols.) were dissolved in ethanol (50 c.c.) at 35—40° and kept at room temperature for 3 days, during which a few crystals (0·03 g.) of (VI) had separated. The alcoholic solution was taken to dryness; extraction of the residue with a little benzene left a further 0·01 g. of (VI) undissolved. These fractions of (VI), once recrystallised from benzene, had m. p. 221—222°. From the alcoholic solution was recovered a mixture of (IV) and (V), m. p. 130—135°, and a small quantity of unchanged *trans*-*p*-$C_6H_4Me{\cdot}NH_2,PPr^n_3,PtCl_2$. An attempt to investigate this equilibrium spectrophotometrically with a Unicam S.P. 500 instrument showed that, in very dilute solution ($1{\cdot}14 \times 10^{-5}$M) even with 100% excess of *p*-toluidine, it lies entirely on the side of free *p*-toluidine. The absorption spectrum of a mixture of (VI) ($0{\cdot}57 \times 10^{-5}$M) with 100% excess of *p*-toluidine ($1{\cdot}14 \times 10^{-5}$M) in ethanol was identical with that calculated from the spectrum of the components, and remained unchanged for 18 hr., showing that no reaction had occurred. Further work along these lines is proceeding; our preliminary results indicate, however, that the reaction between *p*-toluidine and the tetrachloro-compound (VII) is a fairly rapidly established equilibrium lying entirely on the side of free *p*-toluidine at low concentrations (10^{-5}M).

Isomerisation of (IV) *and* (V).—The compound (IV) (0·25 g.) was boiled under reflux for 15 hr. and then taken to dryness, leaving a mixture, m. p. 138—148°, of (IV) and (V) containing about 35% of (V) (estimated spectrophotometrically in a $1{\cdot}11 \times 10^{-5}$M-solution in alcohol). Under the same conditions (V) (0·245 g.) was recovered almost unchanged. It had m. p. 123·5—124·5°, mixed m. p. 124—124·5°, and after one recrystallisation melted at 125—126°. A trace of tri-*n*-propylphosphine caused rapid isomerisation of (IV) in benzene at room temperature.

Isomerisation of (VIII).—The dielectric constant of a solution of (VIII) (0·4264 g.) in benzene (56·88 g.) was measured at 25° after various times. The dielectric constant (ε) decreased, approaching a constant value in about 25 hr. The value at zero time, found by extrapolation, was used to determine the dipole moment of (VIII) (t = time in min. from making up of the solution) :

t	0	15	20	37	43	55	66	85	104
ε	(2·4018)	2·4003	2·3997	2·3983	2·3979	2·3971	2·3965	2·3955	2·3947
t	136	190	19 hr.	25 hr.					
ε	2·3935	2·3923	2·3886	2·3884					

This change in dielectric constant is attributed to isomerisation in solution, to yield the *trans*-isomer, and corresponds to about 10% isomerisation in 25 hr.

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[*Received, March 21st,* 1953.]

483. *Organometallic and Organometalloidal Fluorine Compounds. Part VIII.* The Electrochemical Fluorination of Dimethyl Sulphide and Carbon Disulphide.*

By A. F. Clifford, H. K. El-Shamy, H. J. Emeléus, and R. N. Haszeldine.

Electrochemical fluorination of dimethyl sulphide in anhydrous hydrogen fluoride yields the compounds $CF_3{\cdot}SF_5$ and $(CF_3)_2SF_4$. Carbon disulphide similarly gives the compounds $CF_3{\cdot}SF_5$, $CF_2(SF_5)_2$, and $CF_2(SF_3)_2$. Attempts to fluorinate the corresponding selenium compounds were unsuccessful.

The process for the electrochemical fluorination of organic compounds developed by Brice, Dresdner, Francis, Harland, Hogg, Pearlson, Simons, and Wilson (*Trans. Electrochem. Soc.*, 1949, **95**, 47) has been widely applied to the preparation of fully fluorinated compounds: it has not, as yet, been examined as a method for converting organometallic or organometalloidal compounds into their fluorocarbon analogues, and this paper records the beginning of investigations in this direction.

Two sulphur compounds, dimethyl sulphide and carbon disulphide, were chosen, since bistrifluoromethyl sulphide, a possible reaction product from dimethyl sulphide, has been characterised earlier (Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198), and the reaction of carbon disulphide with cobalt trifluoride has been found by Silvey and Cady (*J. Amer. Chem. Soc.*, 1950, **72**, 3624) to yield trifluoromethylsulphur pentafluoride. The experiments described below have been made mainly to develop and test a convenient laboratory cell for electrolysis in hydrogen fluoride, and no attempt has been made to examine the effect of the concentration of solute, temperature, applied voltage, current density, etc., on the yield. The experiments with dimethyl sulphide have demonstrated the possibility of converting the $S{\cdot}CH_3$ group into $S{\cdot}CF_3$ directly, even though extensive cleavage occurs and carbon tetrafluoride and sulphur hexafluoride are major products. The less volatile products, $CF_3{\cdot}SF_5$ and $(CF_3)_2SF_4$, constituted 20 and 2% respectively of the gas liberated from the cell, and the former was shown to be identical with the compound obtained by Silvey and Cady (*loc. cit.*). Bistrifluoromethylsulphur tetrafluoride has a vapour pressure in the temperature range $-40°$ to $+20°$ expressed by the equation $\log_{10} p(\text{mm.}) = 7{\cdot}027 - 1217{\cdot}6/T$, whence the boiling point is 20·5°, the latent heat of vaporisation is 5·57 kcal./mole, and Trouton's constant is 19·0.

There is as yet no full understanding of the electrode processes involved in electrolysis in anhydrous hydrogen fluoride. It is to be noted, however, that the electrolysis products contained sulphur in its highest valency state. Careful examination was made for bistrifluoromethyl sulphide, but this was not a reaction product. Conversion of the sulphur into the sexavalent state must occur at an early stage in the electrolysis [*e.g.*, by formation of $(CH_3)_2SF_4$, $(CHF_2)_2SF_4$, etc.] to give compounds which remain soluble in hydrogen fluoride and then undergo complete replacement of hydrogen by fluorine. Replacement of hydrogen by fluorine initially would give bistrifluoromethyl sulphide which, like perfluorodimethyl ether, is insoluble in hydrogen fluoride and would be collected as a reaction product. Carbon–sulphur bond fission thus probably occurs in the later stages of the electrolysis.

Carbon disulphide yielded trifluoromethylsulphur pentafluoride, in agreement with the recent work of Silvey and Cady (*ibid.*, 1952, **74**, 5792), but in addition small yields of the new compounds $CF_2(SF_5)_2$ and $CF_2(SF_3)_2$ were isolated. Secondary reactions also occurred, since free sulphur was deposited in the cell. The vapour pressure of difluoromethylenebis(sulphur pentafluoride) is expressed by the equation $\log_{10} p(\text{mm.}) = 7{\cdot}423 - 1516{\cdot}1/T$ between 23° and 36°, whence the boiling point is 60·5°, the latent heat of vaporisation is 6·93 kcal./mole, and Trouton's constant is 20·8. The compound is immiscible with carbon disulphide at low temperature and only partly miscible at room temperature. It is immiscible with ethanol at room temperature and completely miscible with trifluoromethyl sulphur pentafluoride. Like sulphur hexafluoride and trifluoro-

* Part VII, Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

methylsulphur pentafluoride, difluoromethylenebis(sulphur pentafluoride) is inert to sodium ethoxide solution at 100°. Only small amounts of difluoromethylenebis(sulphur trifluoride) (b. p. 35°) were isolated, and it is again apparent that electrochemical fluorination, like reaction with elementary fluorine, yields compounds with sulphur in its highest valency state.

Preliminary experiments with dimethyl selenide and carbon diselenide showed that extensive decomposition occurred on electrolysis; selenium was deposited on the electrodes and then, with carbon diselenide, no current could be passed.

The ultra-violet spectra of the compounds $CF_3 \cdot SF_5$ and $CF_2(SF_5)_2$ are tabulated and their infra-red spectra are reported in the Experimental section.

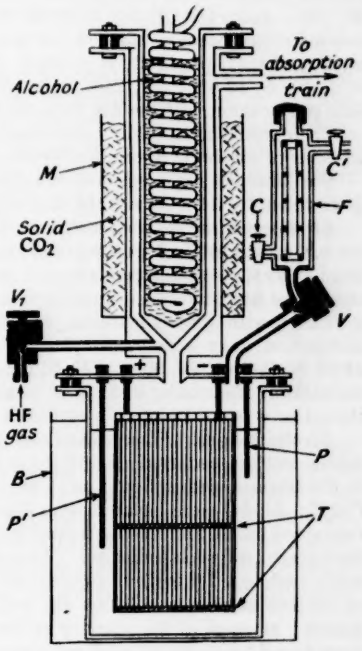
Ultra-violet spectra.

$CF_3 \cdot SF_5$	$\lambda_{max.}$ 228, ε, 5·6; $\lambda_{min.}$ 225·5, ε, 2·8.
$CF_2(SF_5)_2$	General absorption: ε_{240} 2, ε_{230} 2·5, ε_{220} 2·9, ε_{210} 8·5.

Experimental

Apparatus.—The electrolytic cell employed is shown diagrammatically in the Figure. It is based on that described by Simons (" Fluorine Chemistry," Vol. I, Academic Press Inc., p. 417), but several improvements and modifications make it suitable for laboratory research as distinct from use in an industrial process.

The body of the cell was a flanged nickel cylinder, 15 cm. long and 8 cm. in diameter, closed at the bottom by a silver-soldered nickel disc. The electrode assembly consisted of 26 nickel sheets (each 12·7 × 6·3 × 0·08 cm. thick) as alternate anodes and cathodes. The electrodes were insulated from each other by Teflon spacers (*T*), and were suspended from the nickel lid of the cell by their leads, which were also insulated by Teflon bushings. The lid was secured to the flange of the cell body by 12 bolts and was rendered leakproof by a 0·3-cm. Teflon gasket. In addition to the main electrode system the lid carried two insulated electrical probes (*P*, *P'*), which extended to $\frac{1}{3}$ and $\frac{2}{3}$ of the depth of the cell respectively, and were used to determine the electrolyte level. A cylindrical chamber (*F*) of 65-ml. capacity, fitted with a polychlorotrifluoroethylene window, was silver-soldered to the lid and fitted with inlet and exit valves (*C*, *C'*) by means of which it could be flushed with dry nitrogen. This chamber was used for the gradual addition of solute through the nickel needle valve (*V*) (packed with Teflon). In the centre of the lid was an exit tube leading to a condenser, the cold finger of which was 16 cm. long, 4 cm. in diameter, and 0·7 cm. from the outer tube of the condenser. The cold finger was filled with alcohol and cooled to −10° by a coil through which brine was circulated. An outer vessel *M* was filled with solid carbon dioxide when the cell was being filled with hydrogen fluoride (500 ml. of liquid) though valve V_1. The hydrogen fluoride used was sufficiently anhydrous to render a preliminary electrolysis unnecessary. The cell was cooled externally to 0° during electrolysis by immersion in the cooling bath *B*.



Laboratory cell for electrochemical fluorination in anhydrous hydrogen fluoride.

Solutions of dimethyl sulphide and selenide were sufficiently conducting, but, in experiments with carbon disulphide and diselenide, 1—2 g. of sodium fluoride or barium fluoride were added to increase the conductivity. The average operating conditions were 3·5—5 amp. at 5 v, with a current density *ca.* 0·0025 amp./sq. cm.

A nickel tube led from the top of the condenser to the absorption train, all joints in the metal parts of which were silver soldered. The first tube in the train was of brass (60 × 5 cm.) and

was filled with sodium fluoride pellets to remove hydrogen fluoride from the exit gases. The second tube (of glass) was inserted to remove fluorine monoxide which might arise from traces of moisture entering the electrolyte during operation. Initially this tube was filled with cobalt carbonate, but in later experiments a packing consisting of lengths of small-bore rubber tubing was preferred since contamination of the products by carbon dioxide was thereby avoided. In the experiments with carbon disulphide a further tube packed with piperazine was inserted to remove traces of carbon disulphide vapour. The volatile reaction products were then condensed from the hydrogen stream (the cathode gas) by three traps cooled in liquid air and protected by a phosphoric oxide guard tube; these products were transferred to a vacuum system for purification.

Electrochemical Fluorination of Dimethyl Sulphide.—The cell was charged with redistilled dimethyl sulphide (16·9 g.) and hydrogen fluoride (500 ml.), further additions of which were made from time to time to maintain the electrolyte level. Electrolysis was started with a current of 6·5 amp., which fell to 3·5 amp. during the experiment. After 15 hr. a rapid decrease in current was apparent, indicating the completion of the electrolysis. The reaction products were washed with 10% aqueous sodium hydroxide, dried (P_2O_5), and fractionated to give carbon tetrafluoride and sulphur hexafluoride, identified by molecular-weight and infra-red spectroscopic measurements; these compounds were 58 and 17%, respectively, of the total gaseous products. Two less volatile products were isolated: The first was trifluoromethylsulphur pentafluoride (30·5 g.; 20% of total product), b. p. −20° (Found: F, 77·0; S, 16·3%; *M*, 196. Calc. for CF_5S: F, 77·5; S, 16·4%; *M*, 196); Silvey and Cady's vapour-pressure measurements were confirmed. The second was *bistrifluoromethylsulphur tetrafluoride* (3·5 g.; *ca.* 2% of total product), b. p. 20·5° (Found: F, 77·3; S, 13·0%; *M*, 243. $C_2F_{10}S$ requires F, 77·3; S, 13·0%; *M*, 246); the products from several experiments were combined for the final purification, but the low Trouton constant may indicate a slight impurity.

Trifluoromethylsulphur pentafluoride was recovered unchanged after 60 hr. at 100° in 20% aqueous or alcoholic potassium hydroxide.

For analysis, the sulphur compounds were fused with sodium at 600°; fluoride was determined by thorium nitrate, and sulphide by use of standard iodine and sodium thiosulphate.

Electrochemical Fluorination of Carbon Disulphide.—Electrolysis of carbon disulphide (55 g.; added in 5-ml. portions during 35 hr.) for 45 hr. by the procedure described above gave trifluoromethylsulphur pentafluoride as the major product (>90% yield), and a small amount of sulphur hexafluoride. Small amounts of a less volatile material were also isolated, and were combined with similar material from two further experiments on the same scale as the above: distillation gave *difluoromethylenebis(sulphur pentafluoride)* (0·5%), b. p. 60·5° (Found: F, 75·1; S, 21·7%; *M*, 303. $CF_{12}S_2$ requires F, 75·0; S, 21·1%; *M*, 304), and difluoromethylenebis(sulphur trifluoride) (0·5%), b. p. 35° (micro) (Found: *M*, 229. Calc. for $C_2F_8S_2$: *M*, 228); the latter was not isolated in sufficient yield for full characterisation.

Electrochemical Fluorination of Dimethyl Selenide and Carbon Diselenide.—Extensive decomposition occurred during these experiments, and no selenium compounds were collected in the traps cooled in liquid air. Small amounts of methyl fluoride (Found: *M*, 37. Calc. for CH_3F: *M*, 34) were isolated from dimethyl selenide. The cell contained a black residue which contained nickel and selenium after the dimethyl selenide experiment, and anodic decomposition during electrolysis is indicated. Decomposition is not caused by solvolysis by hydrogen fluoride, since unchanged dimethyl selenide was recovered at the end of the experiment. On electrolysis of carbon diselenide solution the cell resistance increased rapidly until no current could be passed; reversal of the polarity of the cell did not increase the conductivity, and the electrodes were found to be coated with red selenium.

Ultra-violet and Infra-red Spectra.—The ultra-violet spectra were recorded on a Unicam Spectrophotometer. Silica cells were used, and the extinction coefficient, ε, was given by $\varepsilon = 760 \times 22{\cdot}4 \times DT/273\,lp$, where D = optical density, T = temperature (°K), l = cell length (cm.), and p = pressure (mm.).

Infra-red spectra were taken by a Perkin-Elmer Model 21 Double Beam Instrument with sodium chloride optics; the results were:

$CF_3{\cdot}SF_5$ ..... 3·36, 3·50(vw doublet), 4·03(w), 4·15(m), 4·68(w), 4·88(w), 4·98(w), 5·40(w), 5·66(w), 6·13(w), 6·29(m), 6·60(m), 6·80(w), 7·24(w), 7·45(m), 7·70(s), 7·97(vs), 8·20(s), 8·57(vs), 9·35(w), 9·92(w), 11·10(vs), 11·26, 11·32(m doublet), 13·15, 13·24, 13·35(vs triplet), 14·40, 14·50(vs doublet).

$(CF_3)_2SF_4$ ... 4·16(m), 6·70(m), 6·87(m), 7·50(m), 7·70(s), 7·94(vs), 8·64(s), 9·29(m), 10·15(m), 11·08(s), 11·67(s), 12·21(m), 13·24—13·45(s), 14·44—14·57(s).

$CF_2(SF_5)_2$ ... 4·17(w), 6·33(m), 6·45(m), 6·60(m), 8·12(vs), 8·47(vs), 8·82(s), 9·05(m), 10·1(m), 10·83(vs), 11·33(vs), 12·5(vs), 13·6(w), 14·5(s).

m = medium, s = strong, vs = very strong, w = weak.

Grateful acknowledgment is made to the Imperial Smelting Corporation Ltd., Avonmouth, for the gift of a cylinder of high-grade anhydrous hydrogen fluoride. One of the authors (A. F. C.) is indebted to the Trustees of the Guggenheim Foundation for the award of a Fellowship.

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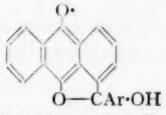
484. *The Unsaturation Energies of Aroxyl Radicals.*

By N. S. HUSH.

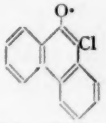
The changes of unsaturation energy on formation of aroxyl radicals from the corresponding phenols by homolytic fission of the O–H bond are discussed on the basis of assumptions similar to those of Diatkina and Syrkin (*Acta Physicochim., U.R.S.S.*, **1946**, **21**, 921) for quinone–quinol systems, and also in terms of a more complete treatment. The results suggest that the critical potentials of phenols determined by Fieser (*J. Amer. Chem. Soc.*, **1930**, **52**, 5204) afford a reasonable measure of the differences in normal potential and of $D_{O\cdots H}$ for these molecules.

Formation of Aroxyl Radicals.—Free radicals are formed by oxidation of monohydroxy-aromatic compounds under a variety of conditions, and in some cases can be isolated (Goldschmidt and Stiegerwald, *Annalen*, 1924, **438**, 202; Goldschmidt, Vogt, and Bredig, *ibid.*, 1925, **445**, 123; Scholl, *Ber.*, 1931, **64**, 1158). There is, moreover, considerable chemical evidence for the view (Conant and Pratt, *J. Amer. Chem. Soc.*, **1926**, **48**, 3220) that, for a number of oxidants, the initial step in oxidation of phenols in solution under not too drastic conditions usually involves formation in an aroxyl radical (cf. Goldschmidt *et al.*, *Ber.*, 1922, **55**, 3197; Pummerer *et al.*, *Ber.*, 1914, **47**, 1472; 1926, **59**, 2161. For later references, see Cosgrove and Waters, *J.*, 1951, 1726). It is true that most of this evidence involves inferences from the structures of the bimolecular products obtained; recent work by Szwarc and Williams (*J. Chem. Phys.*, 1952, **20**, 1171), however, indicates that $D_{\geq C\cdots H}$ in aromatic systems is of the same order as $D_{CH_3\cdots H}$, and as $D_{O\cdots H}$ will certainly be less than this in molecules of this type, initial hydrogen abstraction should generally produce an aroxyl rather than a hydroxyaryl radical.

Oxidation Potentials of Hydroxy-aromatic–Aroxyl Systems.—In this paper, we examine the question of how the overall energy change of this initial hydrogen abstraction step varies with change of aromatic structure of the phenol. The energy changes involved in the oxidation of the corresponding dihydroxy-compounds (quinols) to quinones have been discussed from a theoretical point of view by a number of authors (for references, see Evans and de Heer, *Quart. Reviews*, **1950**, **4**, 94), connection with the actual magnitudes of these quantities being established by means of the gradation of oxidation potentials of quinone–quinol systems.

(I) 

E_0^a = 0·360 v (Ar = phenyl)
0·361 v (Ar = *m*-xylyl)
0·356 v (Ar = *p*-methoxyphenyl)



(II)

E_0^b = 0·85 v

[a] Measurements in alcoholic HCl at 25° (Fieser and Young, *J. Amer. Chem. Soc.*, **1932**, **54**, 4095).
[b] Measurements in 50% alcohol at 25° (Hush, Morgan, and Oldham, unpublished work).

The oxidation potentials of phenol–aroxyl systems, however, are difficult to measure. For a very few radicals, such as anthroxyls of general formula (I) (Scholl, *loc. cit.*) and for 9-chloro-10-phenanthroxyl (II) (Goldschmidt and Stiegerwald, *loc. cit.*), the oxidation

potential can be measured by classical methods, or by simple extensions of them; but, in general, the equilibrium $ArO + \frac{1}{2}H_2 \rightleftharpoons ArOH$ cannot be studied in this way, owing to the lability of the radical. Methods for obtaining a measure of the relative potentials of different phenols were first investigated by Conant (Conant and Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1047; 1924, **46**, 1254; 1927, **49**, 1083; Conant and Pratt, *ibid.*, 1926, **48**, 2468, 3178; Conant, Aston, and Tonberg, *ibid.*, 1930, **52**, 407; Conant, *Chem. Reviews*, 1926, **3**, 1), and were developed by Fieser (*J. Amer. Chem. Soc.*, 1930, **52**, 5204). Attention will be confined in this discussion to Fieser's extensive series of comparative measurements.

For a large number of unstable oxidation–reduction systems, Fieser determined a reproducible quantity which was termed the critical potential (E_c) of the system, and it was suggested that the critical potential measures the reversible potential of the system at a small fixed percentage oxidation, α. The relation between the critical potential and the normal potential E_0 on this hypothesis is then

$$E_c = E_0 + (\boldsymbol{R}T/n\boldsymbol{F}) \ln \alpha/(100 - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the reversible step involves the transfer of n electrons. There is reasonably good evidence in support of this for systems involving two-electron transfer; in all cases studied for which both E_c and E_0 are known, α is approximately 0·5%, corresponding to a value for $(\boldsymbol{R}T/n\boldsymbol{F}) \ln \alpha/(100 - \alpha)$—subsequently referred to for brevity as a—of −0·068 v.

There is unfortunately less direct evidence that equation (1) is also obeyed in the case of one-electron systems. It should be noted, however, that the temperature coefficients of E_c for the phenols are consistent with equation (1) (cf. discussion by Conant and Fieser, *J. Amer. Chem. Soc.*, 1922, **44**, 2480, of entropies of reduction in quinone–quinol systems), and that independent evidence in favour of this relationship is provided by the parallelism between the E_c values of phenols and their chain-breaking capacity as antioxidants in reactions of the type $RO{\cdot}O + ArOH \longrightarrow ROOH + ArO$ (Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 242). More qualitatively, the separation of normal potentials of (I) and (II) roughly parallels that of the E_c values of 9-anthrol and 9-phenanthrol if allowance is made (*e.g.*, by the use of equation 11, below) for the effect of the anthrol–anthrone equilibrium in the former molecule, as would be expected if the difference of aromatic structure is the main reason for the separations both of E_0 and E_c.

Summarizing the position, it appears that the interpretation of the E_c data embodied in equation (1) has some experimental support, but it is by no means conclusive; consequently, these values cannot be used as an unequivocal test of theoretical predictions of the energy changes involved in phenol oxidations. In deciding how to proceed, we must bear in mind that theoretical treatments of the energy changes in quinol ⟶ quinone reactions have been highly successful. It is therefore reasonable to expect that in these simpler and closely analogous systems similar arguments will be equally successful in accounting for the actual variations of the overall energy changes. These calculations may be regarded, in fact, as providing evidence for or against the general applicability of equation (1) to phenol–aroxyl systems.

Energy Changes in the Reaction ArO ⟶ ArOH.—It is necessary to relate the free-energy change ΔG of reaction (*a*) to the change of potential energy ΔE accompanying the

$$ArO_{soln.} + \tfrac{1}{2}H_2 \longrightarrow ArOH_{soln.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

corresponding reaction in the gas phase. Since the structural relation between all ArOH–ArO pairs is very similar, and the members of any pair differ little in mass and in moment of inertia, it can be assumed that

$$\Delta G_1 - \Delta G_2 \simeq \Delta E_1 - \Delta E_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

over the range being considered; the corresponding assumption for quinone–quinol systems appears to be well based (cf. Evans and de Heer, *loc. cit.*). The relation between ΔG and ΔE is discussed more fully on p. 2379; here we require only equation (2), from which it is immediately derivable that

$$\boldsymbol{F}E_0 \simeq -\Delta G + \text{const.} \simeq -\Delta E + \text{const.}' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where E_0 is the normal potential of the system.

Total Energy and π-Electron Energy.—The phenoxyl radical and phenol are isoconjugate with (*i.e.*, contain the same number of π-electrons in approximately the same geometrical configuration of atomic *p*-orbitals as) benzyl and the benzyl anion respectively, and the energy change for reaction (*a*) is

$$\Delta E = \Delta D_\sigma - \tfrac{1}{2}D_{H_2} + E_{(n+1)\pi} - E_{n\pi} - 2E_{p_y} \quad . \quad . \quad . \quad . \quad (4)$$

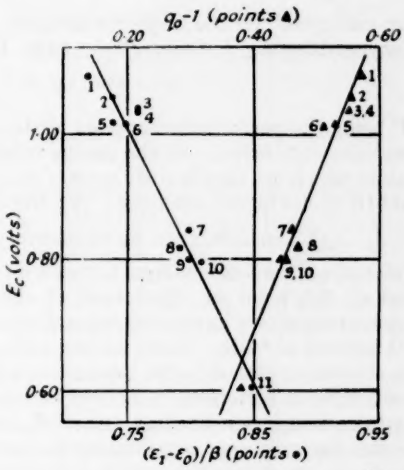
where ΔD_σ is the total change in σ-bond energy of the molecules, E_{p_y} is the energy of an electron in the oxygen p_y orbital with axis of symmetry in the aromatic plane, n is the number of conjugated atomic orbitals, and $E_{(n+1)\pi}$ and $E_{n\pi}$ are the energies of the $n+1$ and n π-electrons of the phenol or aroxyl respectively. Variation in all but these last terms is assumed to be small over a series of conjugated molecules (cf. Evans, Gergely, and de Heer, *Trans. Faraday Soc.*, 1949, **45**, 312); with this assumption, we have

$$\Delta E = E_{(n+1)\pi} - E_{n\pi} + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

This relation, together with (3), leads to the general equation for phenol–aroxyl systems:

$$-\boldsymbol{F}E_0 = \varepsilon_{(n+1)\pi} - \varepsilon_{n\pi} + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the terms in ε are now total π-electron binding energies; and where Fieser's postulate (1) holds, the left-hand side of (5) may be replaced by $\boldsymbol{F}E_c$ + const.'. Equation (5) thus



Potentials measured in 37% EtOH at 25°, referred to the normal hydrogen electrode in this solvent. Directly calculated values of $(\varepsilon_1 - \varepsilon_0)$ were taken from the collections of Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) and of Diatkina and Syrkin (*Acta Physiochim. U.R.S.S.*, 1946, **21**, 641); where direct values are not available, those obtained from the linear relationship between $(\varepsilon_1 - \varepsilon_0)$ and the coefficient of the non-bonding M.O. at the extracyclic atom (Hush, *J.*, 1953, 684) have been employed.

The phenols are numbered as follows: (1), phenol; (2), 2-phenanthrol; (3), *o*-hydroxydiphenyl; (4), *p*-hydroxydiphenyl; (5), 2-naphthol; (6), 4-phenanthrol; (7), 1-phenanthrol; (8), 2-anthranol; (9), 9-phenanthrol; (10), 1-naphthol; (11), 1-anthranol.

permits of a correlation between the oxidation–reduction potential of a monohydroxy-aromatic molecule and the change in π-electron energy accompanying its formation from the corresponding aroxyl radical.

Aromatic Methyl Approximation.—As a first approximation to the calculation of $\Delta\varepsilon$,* the unsaturation energy of the aroxyl radical will be set equal to that of the corresponding aromatic methyl radical (ε_1), and the conjugation energy of the hydroxyl group to the aromatic nucleus will be taken to be roughly constant, so that the unsaturation energy of the phenol will be set equal to that of the aromatic residue (ε_0) plus a constant term. The required difference in unsaturation energy on this approximation is thus

$$\Delta\varepsilon = \varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = (\varepsilon_0 - \varepsilon_1) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

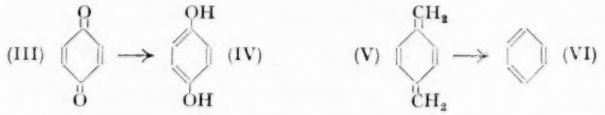
On combination with equation (3), this yields

$$\boldsymbol{F}E_0 = (\varepsilon_1 - \varepsilon_0) + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The plot of E_c against $(\varepsilon_1 - \varepsilon_0)$, in units of the C–C resonance integral, β_{CC}, is shown in the Figure. As would be expected in the relation (1) is valid, this is reasonably linear, and the sign of the slope is in agreement with equation (7); the more highly stabilized the

* Unsaturation energies are calculated on the basis of L.C.A.O. M.O. assumptions, with neglect of non-orthogonality of adjacent atomic orbitals.

radical, the lower the O–H bond-dissociation energy (and E_c) for the phenol. The trend parallels that of quinone–quinol potentials on the similar "quinonedimethane" approximation of Syrkin and Diatkina (*loc. cit.*), in which $\Delta\varepsilon$ for reactions of the type (III) ⟶ (IV) is taken to be identical with that for (V) ⟶ (VI). It is important that the experimental slopes $n\boldsymbol{F}\delta E/\delta(\Delta\varepsilon)$ for the two types of systems are in reasonable agreement with each other.



Influence of Perturbation Terms.—Absolute calculations of unsaturation energies of ArOH and ArO molecules within the framework of M.O. theory are not possible unless the values of all coulomb and resonance integrals for the systems are known. There is, however, much uncertainty as to the correct values of these terms for hetero-atoms, so complete solution of the secular equations would not be particularly informative.

As a first approach to a more complete treatment, the approximate $\Delta\varepsilon$ change accompanying reaction (*a*) will be calculated by a first-order perturbation method. Where $\varepsilon_0{}^j$ is the energy of a π-electron in the M.O. Ψ^j of the isoconjugate hydrocarbon ($\Psi^j = \sum_r c_r{}^j\phi_r$), the energy ε^j in the oxygen-containing molecule is, to first-order approximation (cf. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265),

$$\varepsilon^j = \varepsilon_0{}^j + \sum_r \sum_s c_r{}^{*j} c_s{}^j \int \phi_r{}^* H' \phi_s \mathrm{d}\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

H' being the perturbation applied to the one-electron Hamiltonian of the hydrocarbon by oxygen substitution. Of the energy integrals under the double sum, only three will have values which are significantly greater than zero in each molecule; these are, for the phenol and its isoconjugate analogue: (*x*), the difference in coulomb integral between –OH and $-CH_2^-$, (*y*), the difference in resonance integral for $\rangle C{-}OH$ and $\rangle C{-}CH_2^-$, and (*z*), the difference in coulomb integral between a ring carbon atom in the isoconjugate hydrocarbon and at the point of attachment of –OH in the oxygen-substituted molecule. For the aroxyl radical, we have a corresponding set (*x'*), (*y'*), (*z'*), where the oxygen centre is now –O instead of –OH. Since we are interested in the change of unsaturation energy when an electron is placed in the lowest available orbital of an aroxyl, only those terms which contribute to variations in $\Delta\varepsilon$ need be taken into account; this orbital, in the isoconjugate hydrocarbon, is non-bonding, and it follows immediately * that of the above six perturbation terms, the only one contributing to variation in $\Delta\varepsilon$ is that in *x*; summing over all π-electrons, we obtain the very simple relationship

$$\varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = q_0 x + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where q_0 is the π-electron density at the extracyclic position in the carbanion isoconjugate with the phenol. On combination with equation (5), this yields

$$\boldsymbol{F}E_0 = -q_0 x + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If the connection between the critical potential and the normal potential of phenol–aroxyl systems embodied in Fieser's postulate (1), and equation (10), are valid, the plot of E_c against q_0 should be linear, with a slope of $-x/\boldsymbol{F}$; since –OH is more electron-attracting than $-CH_2^-$, *x* will be negative, so the slope will be positive. The plot of q_0 against E_c for all systems for which potential data are available is shown in the Figure; it is seen that there are no serious deviations from linearity over this range of molecules, and that the slope is indeed positive, as predicted. The relationship between E_c and q_0 is best satisfied by

$$E_c = 3{\cdot}0(q_0 - 1) - 0{\cdot}55 \text{ v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The use of first-order perturbation theory limits the discussion to small values of the hetero-parameters. It can easily be shown, however, that a treatment which is valid over

* The properties of non-bonding orbitals have been described by Longuet-Higgins (*loc. cit.*). Only alternant molecules are considered here.

a larger range of these terms leads to a similar prediction of simple dependence of E_0 on q_0, with the difference that the parameter x of equation (10) becomes a more complex quantity. The conjugation of a hetero-atom to an alternant system has been discussed in detail by Coulson and de Heer (*Trans. Faraday Soc.*, 1951, **47**, 681; *J.*, 1952, 483). Where the hetero-atom is –O(H), contributing two π-electrons, then on the assumptions that x is not too small and that the inductive effect of the hetero-atom on the coulomb term of the carbon atom to which it is attached is approximately constant over a series of structures, it may be derived from the work of these authors that

$$\varepsilon_{\text{conj.}}(-\text{OH}) = 0{\cdot}67\sqrt{\pi_{\text{ii}}}\,(y+1)^2/x^{\frac{1}{2}} + \text{const.} \quad . \quad . \quad . \quad . \quad (12)$$

where $\varepsilon_{\text{conj.}}(-\text{OH})$ is the conjugation energy across the >C–OH bond and π_{ii} is the self-polarizability of the carbon centre (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39) to which the hetero-atom is attached. (All energy terms are in units of β_{CC}.)

Where the hetero-atom contributes only one π-electron to the system (as does –O) and where the parameters are of the same order of magnitude as for –OH, the conjugation energy should be given by an expression of the same form as (12), but with a different

$$\varepsilon_{\text{conj.}}(-\text{O}) = 0{\cdot}67\,\xi\sqrt{\pi_{\text{ii}}}\,(y'+1)^2/(x')^{\frac{1}{2}} + \text{const.} \quad . \quad . \quad . \quad . \quad (12')$$

numerical constant; thus, for –O, the relation (12'), where ξ is a constant, will be expected to hold, the important variable terms being assumed to be those in x' and y'. This leads to

$$\varepsilon_{\text{phenol}} - \varepsilon_{\text{aroxyl}} = 0{\cdot}67\sqrt{\pi_{\text{ii}}}\left\{\frac{(y+1)^2}{x^{\frac{1}{2}}} - \frac{\xi\,(y'+1)^2}{(x')^{\frac{1}{2}}}\right\} \quad . \quad . \quad . \quad (13)$$

Combining this with equations (1) and (5), we should therefore expect E_c to be approximately linear with $\sqrt{\pi_{\text{ii}}}$ over a series of aromatic structures, and this is indeed found to be the case. This relation does not need to be discussed further, for over the range of structures considered here, π_{ii} is related to q_0 by $\sqrt{\pi_{\text{ii}}} \simeq 1{\cdot}182 - 0{\cdot}357q_0$, so that the plot in the Figure can also be regarded as a test of this prediction. In this case it is, of course, difficult to predict the sign of the slope, but there is no reason to believe that the observed sign is inconsistent with the theory.

Discussion of O–H *Bond-dissociation Energies in Phenols.*—These considerations of the energetics of the oxidation reactions support the view that the order of critical potentials for the phenols discussed is, within reasonable limits of error, the order of their standard oxidation–reduction potentials. These quantities are of some interest, as it is possible, with their use, to derive approximate values of the O–H bond-dissociation energies in phenol molecules; we note that a (large) error of 0·1 v in E_0 will contribute only ± 0·1 e.v. to the probable error in $D_{\text{O}\cdots\text{H}}$.

The heat Q_a of reaction (*a*) is related to $D_{\text{O}\cdots\text{H}}$ by

$$Q_a = D_{\text{O}\cdots\text{H}} - \tfrac{1}{2}D_{\text{H}_2} + (Q^g_{\text{ArOH}} - Q^g_{\text{ArO}}) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where Q^g_{ArOH} and Q^g_{ArO} are the heats of solution of gaseous phenol and aroxyl, respectively. The term involving these heats of solution will be small; from the data for quinols and quinones (cf. Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 293), and with allowance for the fact that the oxidant possesses only one –OH group, the difference $Q^g_{\text{ArOH}} - Q^g_{\text{ArO}}$ is estimated at 3 kcal. mole^{-1}. From equation 2, the mean entropy change in reaction (*a*) may be taken to be ~ -16 e.u. mole^{-1}, so that $D_{\text{O}\cdots\text{H}}$ can be estimated to a reasonable approximation from the free energy of the oxidation–reduction reaction in solution. For the term a (equation 1) connecting E_c and E_0, Fieser's proposed value (*loc. cit.*, 1930) * $-0{\cdot}14$ v is employed. On substitution in (14), this gives

$$D_{\text{O}\cdots\text{H}} \simeq 23E_c + 57 \text{ kcal. mole}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

* The value of $\frac{1}{2}D_{\text{H}_2}$ is taken as 52·0 kcal. mole^{-1} (Rossini *et al.*, "Selected Values of Properties of Hydrocarbons," 1948).

Typical values of $D_{O\cdots H}$ (in kcal. mole^{-1}) obtained by the use of equation (15) for the more important molecules are shown below :

Molecule	$D_{O\cdots H}$	Molecule	$D_{O\cdots H}$
Phenol	(82) 84 †	2-Naphthol	80
2-Phenanthrol	81	1-Naphthol	75
p-Hydroxydiphenyl	81	1-Anthrol	71

† The point for phenol lies somewhat off the line in the Figure; the value of 84 kcal. mole^{-1} calculated from (11) and (15) is probably a better approximation in this case.

Although the absolute uncertainty is difficult to estimate, these values are unlikely to be seriously in error. It may be noted that extrapolation in the Figure leads to a value of $D_{O\cdots H}$ for the case $(q_0 - 1) = 1$ of 110 kcal. mole^{-1}. In order to connect this approximately with $D_{O\cdots H}$ for methanol, we need to know the difference in hyperconjugation energy between the ethyl radical and the ethyl anion; calculations by Matsen, Robertson, and Chuoke (*Chem. Rev.*, 1947, **41**, 273) lead to a value ≈ -9 kcal. mole^{-1} for this quantity, and on this crude approximation, this would correspond to $D_{O\cdots H}$ in methanol ≈ 101 kcal. mole^{-1}. This is certainly of a reasonable order of magnitude, as $D_{O\cdots H}$ in ethanol is known to be 101 kcal. mole^{-1} (Laidler and Rebbert, *J. Chem. Phys.*, 1952, **20**, 574).

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485. *The Thermodynamic Properties of Methyl Nitrate.*

By PETER GRAY and P. L. SMITH.

The heat capacity C_p of methyl nitrate has been measured from 13° to 295° K. The melting point T_f is 190·2° K. No other transitions or phase changes were observed. The molar latent heat of fusion L_f is 1·970 kcal. and the molar entropy of fusion S_f is 10·36 e.u. The absolute molar entropy of the liquid at 1 atm. and 298° K, $S_{abs.}^{298}$, is 51·86 e.u. and the standard molar entropy of formation ΔS_f is −92·72 e.u. The enthalpy (heat content) difference between 298° K and absolute zero is 8·256 kcal. mole^{-1}. The specific heat at 298° K of liquid methyl nitrate is 37·57 cal. mole^{-1} deg.$^{-1}$ or 0·483 cal. g.$^{-1}$ deg.$^{-1}$.

The values of the thermodynamic functions just derived have been applied to some reactions of methyl nitrate to give values of enthalpy and free energy balances and equilibrium constants in some of its important reactions. Thus, the best value for the standard heat of formation of liquid methyl nitrate ΔH_f^{298} being taken as $-37·2 \pm 0·8$ kcal. mole^{-1}, the standard free energy of formation ΔF_f^{298} is $-9·55 \pm 0·8$ kcal. mole^{-1}, both values referring to 25° c and 1 atm.

The equilibrium constant [ester][water]/[acid][alcohol] of the reaction between pure nitric acid and methyl alcohol by which it is normally prepared is $K = 2·3 \times 10^5$ and the heat liberated $-\Delta H_{est.}$ is 7·08 kcal. mole^{-1}; and from kinetic measurements on the reverse reaction the velocity constant of esterification should be $k_2 = 4 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$ at room temperature. All these values are in agreement with Berthelot's work on ethyl nitrate where esterification was found to be rapid and complete and $\Delta H_{est.}$ was −6·2 kcal. mole^{-1}.

METHYL NITRATE is the simplest of the nitrate esters and its investigation has thrown light not only on its own properties but also on those of its homologues. Because of its explosive character little experimental work on it has been published; its melting point is here recorded for the first time and until the recent war no experimental value was available for its heat of formation.

In order to supply such information direct measurements have been made of the specific heat of pure methyl nitrate from temperatures near the absolute zero to room temperature,

and the corresponding entropy and enthalpy differences have been evaluated from this and from the latent heat of fusion. These results have been used in calculations of the heat of formation at absolute zero, the heat of formation from gaseous atoms, and the standard free energy of formation, and in applications of these to equilibria.

Experimental

Materials.—Pure methyl nitrate was supplied by the Explosives Research and Development Establishment (Waltham Abbey). It was dried over calcium chloride and fractionally distilled at atmospheric pressure. It boiled at 64·6°. The initial and final fractions were rejected. This material had n_D^{18} 1·3760$_5$.

Apparatus.—A thin-walled copper calorimeter containing two resistance thermometers (constantan for temperatures below 22° K and platinum for higher temperatures) was suspended in a conventional cryostat. An outer vacuum-jacket in direct contact with the refrigerant enclosed a helium liquefier of the Simon expansion type, which, however, was not used in this work. Temperatures below 20° K were obtained by controlled pumping in liquid hydrogen. A copper radiation shield was attached to the expansion chamber, and a high vacuum was maintained during measurements.

Automatic temperature control operated between 20° and 60° K and above 90° K, and the rapid-pumping system enabled measurements to be made nearly to room temperatures. These refinements are the essential differences between this apparatus and that described by Parkinson, Simon, and Spedding (*Proc. Roy. Soc.*, 1951, *A*, **207**, 137).

Method.—Methyl nitrate was sealed in a small copper can under 1 atm. pressure of helium. This atmosphere, and a few copper shavings in the can, ensured rapid distribution of heat without undue increase in thermal capacity. Correction for the heat capacity of the copper container and shavings was computed from published data on copper (*e.g.*, Giauque and Meads, *J. Amer. Chem. Soc.*, 1941, **63**, 1897).

Specific heat values were taken under non-adiabatic conditions, *i.e.*, the calorimeter was always slightly above or below the temperature of its surroundings, and the corresponding small linear drifts were observed before and after heating. These drifts were extrapolated to the mid-point of the heating period to yield the exact temperature rise.

The latent heat was obtained by setting the temperature of the calorimeter a few degrees below the m. p. of methyl nitrate and taking one or two heat capacity points, thus increasing the temperature nearly to the m. p. A continuous current was then passed through the heater and a temperature–time plot made. The melting period could clearly be seen, and immediately on the completion of melting further heat capacity points were taken. The total heat supplied for melting could then be computed.

Results

Melting Point.—Methyl nitrate melted quite sharply at 190·2° K (cf. HNO_3, 231° K; $EtNO_3$, 161° K).

Heat of Fusion.—The heat of fusion at 190·2° K was determined as described (see above), and gave :

latent heat of fusion L_f = 1970 cal./mole
entropy of fusion S_f = 10·36 e.u./mole

These values, in agreement with Walden's empirical rule (1908; quoted by, *e.g.*, Glasstone, "Textbook of Physical Chemistry," MacMillan, 3rd Edn.) $L_f \doteqdot 13{\cdot}5T$, are typical of compounds from which transitions below the m. p. and specific heat anomalies are absent (Ubbelohde, *Quart. Reviews*, 1950, **4**, 356). On melting, new modes of motion as well as translation come into play, as the increase of 8 cals. in the molal heat capacity (from 22·7 to 30·6 cal.) shows.

Heat Capacity.—Table 1 and the Figure give the absolute heat capacities C_p of methyl nitrate in cal. deg.$^{-1}$ mole^{-1} measured from 14° to 291° K. The specific heat of solid methyl nitrate increases regularly from its low value at 14° K to its value at the m. p. without any discontinuity. Melting is accompanied by an increase of specific heat and the specific heat of the liquid continues to rise up to 295°, the last temperature at which measurements were made, to the value c_p = 0·483 cal. g.$^{-1}$ deg.$^{-1}$ (C_p = 37·5 cal. mole^{-1} deg.$^{-1}$). From a plot C_p–T smoothed values of the heat capacity were obtained by interpolation, and the derived quantity C/T was calculated from them. These values are listed in Table 2 and are used in calculations of the thermodynamic functions.

TABLE 1. *Molar heat capacity, C_p, of methyl nitrate.*

Temp. (K)	Molar specific heat (cal. mole^{-1} deg.$^{-1}$)	Temp. (K)	Molar specific heat (cal. mole^{-1} deg.$^{-1}$)	Temp. (K)	Molar specific heat (cal. mole^{-1} deg.$^{-1}$)	Temp. (K)	Molar specific heat (cal. mole^{-1} deg.$^{-1}$)
Series I.	0·1085 *mole.*	*Series* I.	0·1085 mole.	*Series* II.	0·268 *mole.*	*Series* II.	0·2680 *mole.*
13·95°	0·985	44·6°	7·45	93·0°	14·3	216·5	33·5
14·45	1·05	45·3	8·30	95	14·3		
15·07	1·18	46·1	8·30			230	35·0
15·77	1·34			100·6	15·0		
16·6	1·53	52·9	8·94	102·7	14·8	244	35·9
17·94	1·85	54·1	9·40	104·9	15·1		
19·11	2·22					265·3	36·8
		62·7	10·2	121·5	16·6		
20·16	2·35	64·6	10·4	123·5	16·6	277	37·5
21·57	2·62	66·4	10·6				
22·92	2·86			138	18·4	295·5	37·3
24·60	3·25						
26·16	3·72			151·2	19·1	*Series* III.	0·2534 *mole.*
28·22	4·25			152·9	19·5	193·7°	31·17
33·05	5·03			174·5	21·4	200	32·17
34·35	5·83			179·5	22·8	204·4	32·60
35·3	6·96					207	32·92
36·4	6·91			181·0	23·0		
37·45	6·82						
38·3	6·82			190·2 = Melting point.			

TABLE 2. *Heat capacity, C_p, of methyl nitrate. Interpolated values of C_p and C_p/T taken from smoothed plot of C_p–T (see Figure).*

Temp. (K) (T)	Specific heat (cal. mole^{-1} deg.$^{-1}$) (C_p^{solid})	C_p/T	Enthalpy difference (cal. mole^{-1}) $H(T)-H(0)$	Entropy difference (cal. mole^{-1} deg.$^{-1}$) $S(T)-S(0)$	Temp. (K) (T)	Specific heat (cal. mole^{-1} deg.$^{-1}$) (C_p^{liquid})	C_p/T	Enthalpy difference (cal. mole^{-1}) $H(T)-H(0)$	Entropy difference (cal. mole^{-1} deg.$^{-1}$) $S(T)-S(0)$
	Solid.					*Liquid.*			
20°	2·40	0·110	13·35	0·840	190·2°	Fusion	—	$L_f = 1970$	$S_f = 10{,}360$
25	3·30	0·132	—	—	190·2	30·60	0·160	4483	35,960
30	4·55	0·152	—	—					
35	6·05	0·173	—	—	200	32·05	0·160	4759	37,370
40	7·30	0·183	107·05	3,924	210	33·17	0·158	—	—
45	8·20	0·182	—	—	220	34·07	0·155	5422	40·530
50	8·95	0·179	—	—	230	34·90	0·152	—	—
60	10·25	0·171	282	7,498	240	35·60	0·148	6120	43,560
70	11·55	0·165	—	—	250	36·15	0·145	—	—
80	12·65	0·158	509	10,774	260	36·60	0·141	6842	46,450
90	13·75	0·153	—	—	270	36·96	0·137	—	—
100	14·75	0·147	785	13,816	280	37·25	0·133	7581	49,270
110	15·67	0·143	—	—	290	37·45	0·129	—	—
120	16·52	0·138	1100	16,656					
130	17·50	0·135	—	—	291·2	37·48	0·1285	7992	50,710
140	18·40	0·131	1453	19,348	298·2	37·57	0·126	8256	51,860
150	19·35	0·129	—	—					
160	20·25	0·127	1841	21,912					
170	21·10	0·124	—	—					
180	21·90	0·122	2263	24,376					
190	22·65	0·119	—	—					
190·2	22·70	0·119	2513	25,596					

Difference between Heat Content at Absolute Zero and Room Temperature.—Calculation of the enthalpy difference between 0° and 298·1° K is shown in Table 3.

TABLE 3. *Calculation of the molar enthalpy of methyl nitrate relative to absolute zero.*

	Cal. deg.$^{-1}$
Debye's T^3 law, 0—13·95° K	3·46
Graphical integration, 13·95—190·2° K	2510
Fusion at 190·2° K	1970
Graphical integration, 190·2—298·1° K	3773
Total $H^{298}-H^0$	8256

The calculation is made partly from numerical integration on the assumption that Debye's T^3 law holds below 14° K, and the remainder from the latent-heat term and a graphical integration of the area between the C_p curve and the T axis. The difference in enthalpy between 0° and 298·1° K is 8156 cal. mole^{-1}.

Entropy from Calorimetric Data.—Table 4 illustrates an entropy calculation, which is made partly from the Debye T^3 law below 14° K, the remainder from the latent-heat term and an integration of the area between the plot of C_p/T and the T axis. The "absolute entropy" per mole of liquid methyl nitrate at 25° C is $S_{abs.}^{298} = 51{\cdot}86$ cal. mole^{-1} deg.$^{-1}$.

Molar heat capacity of methyl nitrate from 14° to 298° K.

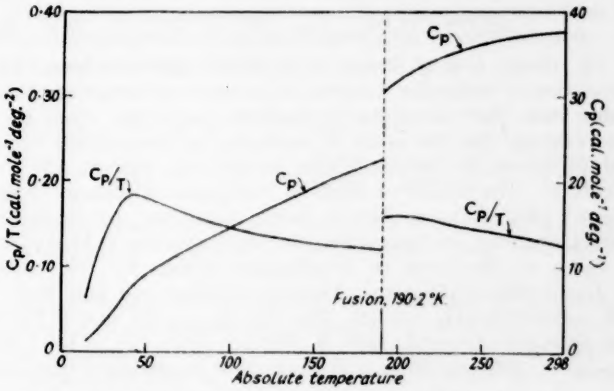

TABLE 4. *Calculation of the entropy of methyl nitrate relative to absolute zero ("absolute entropy").*

	e.u.
Debye's T^3 law, 0—13·95° K	0·328
Graphical integration, 13·95—190·2° K	25·268
Fusion, 1970/191·2	10·36
Graphical integration, 191·2—298·1° K	15·90$_4$
Total ($S^{298\cdot1}$)	51·86

The entropy of formation in the standard state from its elements is thus:

$$\Delta S_f^{298} = S_{CH_3\cdot NO_3}^{298} - \Sigma S_{elements} = 51{\cdot}86 - 144{\cdot}58\ *$$
$$\Delta S_f^{298} = -92{\cdot}72 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

DISCUSSION

The values of the thermodynamic functions just derived may be applied to the reactions of methyl nitrate to give quantitative information about the enthalpy and free energy balances in some of its important reactions and to enable equilibrium constants to be evaluated.

Thermochemical Properties.—(1) *Standard heat of formation of methyl nitrate.* This fundamental quantity has been the subject of only one published determination. Experiments made at Woolwich Arsenal on the heats of explosion of various substances (Whittaker, Wheeler, and Pike, *J. Inst. Fuel*, 1947, **20**, 137) gave for methyl nitrate the value:

$$Q_{explosion} = 1640 \pm 10 \text{ cal. g.}^{-1}$$

from which

$$\Delta H_f^{298} = -37{\cdot}2 \pm 0{\cdot}8 \text{ kcal. mole}^{-1}$$

for the heat of formation of liquid methyl nitrate. From this value and from the enthalpy differences of the elements between absolute zero and room temperature the value of the heat of formation at absolute zero of methyl nitrate, ΔH_f^0, may be deduced:

$$\Delta H_f^0\ (CH_3\cdot NO_3) = -37{\cdot}200 - 8{\cdot}256 + 7{\cdot}443\ \dagger = -39{\cdot}8 \pm 0{\cdot}8 \text{ kcal. mole}^{-1}$$

* S^{298} for the elements are taken from *J. Res. Nat. Bur. Stand.*, 1945, **34**, 143) as C (graphite) 1·374, 1·5H_2 46·816, 0·5N_2 2·883, and 1·5O_2 73·504, total 144·58 cal. mole^{-1} deg. (c)$^{-1}$.

† From the following values for $H^{298\cdot1} - H^0$ (cal.): $CH_3\cdot NO_3$ 913·1; C (graphite) 251·56; 1·5H_2 3050·71; 1·5O_2 3104·67; 0·5N_2 1036·13; total for elements 7443.

(2) *Heat of formation of methyl nitrate vapour.* The latent heat of vaporisation of methyl nitrate has been variously reported. A recent redetermination by Moelwyn-Hughes and McKinley-McKee (*Trans. Faraday Soc.*, 1952, **48**, 247) of the variation of vapour pressure with temperature gives $L = 7730$ cal. mole^{-1} in near agreement with the figure $L = 7800$ cal. mole^{-1} obtained by Thomson and Purkis (*ibid.*, 1936, **32**, 674). Thus the heat of formation of gaseous methyl nitrate at 298° c is

$$\Delta H_f^{298}\ (CH_3{\cdot}NO_{3\,g}) = -37{\cdot}2 + 7{\cdot}77 = -29{\cdot}4 \pm 0{\cdot}8 \text{ kcal. mole}^{-1}$$

(3) *Atomic heat of formation of methyl nitrate vapour.* In explosives chemistry the correlation of molecular structure with heats of formation of compounds in their standard states from their elements in standard states has often been attempted. It has the disadvantage that the heats of formation are numerically small, and experimental errors and variations in intermolecular forces may obscure the variations due to chemical structure. The values of heats of formation of gaseous compounds from their isolated atoms, ΔH_a, form a better basis, according to Springall and Roberts (personal communication), for comparison and interpretation of behaviour.

Some of the heats of atomisation needed for the calculations are still disputed. A. G. Gaydon ("Diatomic Molecules," Chapman and Hall, London, 1947) has given $\Delta H = 103{\cdot}22$ for $H_2 \longrightarrow 2H$, 225·1 for $N_2 \longrightarrow 2N$, and 117·2 kcal. mole^{-1} for $O_2 \longrightarrow 2O$, and Springall (*Research*, 1950, **3**, 260) has given $\Delta H = 136{\cdot}1$ kcal. mole^{-1} for $C_{graphite} \longrightarrow C_{gaseous}$. Combining these with the heat of formation of gaseous methyl nitrate gives :

$$\Delta H_a^{298}\ (CH_3{\cdot}NO_{3\,g}) = -608{\cdot}7 \text{ kcal. mole}^{-1}$$

(4) *Free energy of formation from the elements in their standard state.* From the value determined for the entropy of liquid methyl nitrate at 25° c its standard free energy of formation may be deduced from its known heat of formation.

Since $\Delta H_f^{298} = -37{\cdot}2 \pm 0{\cdot}800$ kcal. mole^{-1}
and $\Delta S_f^{298} = -88{\cdot}20$ cal. mole^{-1} deg.$^{-1}$
we find $\Delta F_f^{298} = -9{\cdot}55 \pm 0{\cdot}8$ kcal. mole^{-1}

Reaction between Methyl Alcohol and Nitric Acid and the Hydrolysis of Methyl Nitrate.—Methyl nitrate being made by esterification of methyl alcohol, it is important to know the thermodynamic functions for this reaction (no experimental work has yet been done on it). Values may be estimated for the enthalpy and free-energy changes (and hence the equilibrium constant) of the reversible reaction between pure components. By applying data obtained from measurements on the hydrolysis of methyl nitrate estimates may be made of the corresponding reaction in aqueous solution and of the energies of activation and velocity constants of esterification. At present their accuracy is limited by the accuracy of the Woolwich value $37{\cdot}2 \pm 0{\cdot}8$ kcal. for the molar heat of formation of liquid methyl nitrate.

(1) *Thermodynamic properties.* (*a*) Pure liquids. Inserting the values derived above and others tabulated [Nat. Bur. Standards' values quoted by H. Paul ("Principles of Chemical Thermodynamics," McGraw-Hill, New York, 1951) and F. R. Bichowsky and F. D. Rossini ("Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, 1936)] into the equation for esterification we have :

$$CH_3{\cdot}OH + HNO_3 \rightleftharpoons CH_3{\cdot}NO_3 + H_2O$$

Enthalpy of formation	−57·036	−41·404	−37·2	−68·317	Hence $\Delta H = -7{\cdot}08$
Free energy of formation ...	−39·75	−19·10	− 9·55	−56·69	Hence $\Delta F = -7{\cdot}40$

The enthalpy change on esterification is thus $-7{\cdot}08 \pm 0{\cdot}8$ kcal. mole^{-1} and should be compared with Berthelot's experimental measurement (M. Berthelot, "Sur la force des matières explosives," 1890; transl. Hake and MacNab, Murray, London, 1892) of the heat of esterification of ethyl alcohol by nitric acid, namely, 6·9 kcal. mole^{-1}.

The free energy change of $-7{\cdot}40 \pm 0{\cdot}8$ kcal. mole^{-1} corresponds to a thermodynamic

equilibrium constant K where $\log_{10} K = 5{\cdot}36 \pm 0{\cdot}55$, *i.e.*, $K = 2{\cdot}3 \times 10^5$. Thus at room temperature the equilibrium greatly favours esterification, in accordance with the fact that Berthelot was able to prepare ethyl nitrate in virtually 100% yield at room temperature by running a stream of minute drops of ethyl alcohol into well-stirred, pure nitric acid.

(*b*) Aqueous solutions. If it is assumed that the enthalpy and free energy of methyl nitrate do not differ greatly from conditions of excess of water to equimolar proportions * we may evaluate the thermodynamic properties of the esterification in aqueous solutions.

In aqueous solution the nitric acid is ionised completely :

$$CH_3{\cdot}OH_{aq.} + H^+_{aq.} + NO_3^-{}_{aq.} \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} CH_3{\cdot}NO_{3\,aq.} + H_2O \quad . \quad . \quad . \quad . \quad (A)$$

Enthalpy of formation	−58·79	−49·19	−37·2	−68·32	Hence $\Delta H = +2{\cdot}46$ kcal.
Free energy of formation ...	−41·90	−26·5	− 9·55	−56·69	Hence $\Delta F = +2{\cdot}15$ kcal.

It will be seen that esterification is now endothermic ($\Delta H = 2{\cdot}5 \pm 1$ kcal.), and that hydrolysis is favoured at room temperature ($\log_{10} K' = \bar{2}{\cdot}423 \pm 0{\cdot}6 = -\Delta F^\circ/\boldsymbol{R}T$ corresponding to $K' = 0{\cdot}0265$).

(2) *Kinetic aspects.* In any reversible reaction the ratio of the forward velocity constant k_f to the reverse k_r is equal to the equilibrium constant K; and the difference between the apparent activation energies of forward (E_f) and reverse (E_r) reactions is equal to the enthalpy change ΔH. Thus in reaction (A) (H_2O in excess), we have $k_f'/k_r' = K'$ and $E_f' - E_r' = \Delta H'$. For this equilibrium $K' = 0{\cdot}255$, and $\Delta H' = +2{\cdot}46$ kcal. Moelwyn-Hughes and McKinley-McKee have investigated the hydrolysis and found values for k_r' and E_r' as functions of temperature in the range 70—140° c. Extrapolation of their results gives $E_r' = 29{\cdot}5$ kcal. at 298° K, whence $E_f' = 2{\cdot}5 + 29{\cdot}5 = 32$ kcal. If the hydrolysis is not sensibly different in equimolar proportions and in excess of water, *i.e.*, if $E_r' = E_r$, then $E_f = -7{\cdot}08 + 29{\cdot}5 = 22$ kcal. The uncertainty in the value of velocity constants outside the experimental range is too great for more than an estimate of the speed of esterification. Such estimates may be made however.

At 298° K $k_r'[H_2O] \simeq 10^{-9}$ sec.$^{-1}$, and for the esterification between pure reactants with $K = 2 \times 10^5$ we have $k_f \simeq 4 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$, or $k_f \simeq 10^{11} \exp(-22{,}000/\boldsymbol{R}T)$ mole^{-1} sec.$^{-1}$. Thus we are able from existing data and these thermodynamic measurements to predict velocities of reactions on which no experimental work has been published.

We thank Dr. R. Hill for his kindness in helping us with some of the experimental work, Professor F. Simon and Dr. F. P. Bowden for laboratory and workshop facilities, and Dr. K. G. Denbigh for his comments.

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* Equivalent to assuming zero heat of dilution of methyl nitrate from mole fraction 0·5 to 0.

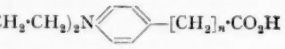
486. *Aryl-2-halogenoalkylamines. Part XII.* Some Carboxylic Derivatives of* NN*-Di-2-chloroethylaniline.*

By J. L. Everett, J. J. Roberts, and W. C. J. Ross.

The preparation is described of a number of derivatives of *NN*-di-2-chloroethylaniline containing carboxyl groups, and the reactivities of their chlorine atoms have been assessed by determining the rates of hydrolysis in aqueous acetone. It is shown that the effect of substituents on the reactivity of the chlorine atom in a series of *NN*-di-2-chloroethylanilines can be expressed by Hammett's equation (*J. Amer. Chem. Soc.*, 1937, **59**, 96), ρ having the value −2·10. The activity of a number of the derivatives as tumour-growth inhibitors is briefly discussed.

The study of aryl-2-halogenoalkylamines (" aromatic nitrogen mustards ") has made it clear that most substances which contain a di-2-chloroethylamino-group possessing a certain level of chemical reactivity are cytotoxic to proliferating tissues (Haddow, Kon, and Ross, *Nature*, 1948, **162**, 824; Ross, *J.*, 1949, **183**, and subsequent papers; Ross, *Adv. Cancer Res.*, 1953, **1**, 397). However, their use as chemotherapeutic agents has been limited by their lack of specific action on malignant growths—many normal proliferating tissues are equally affected by most of the derivatives. Danielli (*Nature*, 1952, **170**, 863) has pointed out that cells may be extremely selective in the types of molecule which they concentrate within their plasma membranes. It is hoped to obtain compounds of more selective action on neoplasms by incorporating the di-2-chloroethylamino-group into molecules which have anionic, cationic, lipophilic, of hydrophilic character. The present paper describes the preparation and properties of some carboxyl-substituted derivatives of *NN*-di-2-chloroethylaniline.

A series of acids (I), where $n = 0$—**4**, has been prepared. The first member, *NN*-di-2-chloroethyl-*p*-aminobenzoic acid (I; $n = 0$), and its methyl and ethyl esters, have already



(I) $(Cl\cdot CH_2\cdot CH_2)_2N$—$[CH_2]_n\cdot CO_2H$

been described (Ross, *J.*, 1949, **183**; Everett and Ross, *J.*, 1949, 1972). The methyl or ethyl esters of *p*-aminophenyl-acetic, -propionic, -butyric, and -valeric acids were converted successively into the *NN*-di-2-hydroxyethyl esters, the *NN*-di-2-chloroethyl esters, and the *NN*-di-2-chloroethyl acids by the methods used for preparation of the benzoic acid derivatives (Everett and Ross, *loc. cit.*).

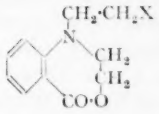
Whilst hydrolysis of methyl *NN*-di-2-chloroethyl-*m*-aminobenzoate yielded the required acid, diethyl *NN*-di-2′-chloroethyl-4-aminophthalate could not be converted into the corresponding dicarboxylic acid since conditions of reaction sufficiently drastic to effect hydrolysis also resulted in decarboxylation to *NN*-di-2-chloroethyl-*m*-aminobenzoic acid.

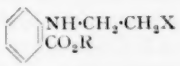
When methyl anthranilate is heated with two equivalents of ethylene oxide in benzene solution at 160° the main reaction product is **2 : 3 : 4 : 7**-tetrahydro-**4**-2′-hydroxyethyl-**7**-keto-**5** : **6**-benz-**1** : **4**-oxazepine (II; X = OH). Methyl *N*-2-hydroxyethylanthranilate (III; X = OH, R = Me) is also formed but none of the required bishydroxyethyl compound (IV; X = OH, R = Me) could be isolated. The monohydroxyethyl compound becomes the sole product when methyl anthranilate is treated with an excess of ethylene oxide in aqueous acetic acid solution. Kiprianov (*Ukrainskii Khem. Zhurnal*, 1925, **1**, 644) claimed to have obtained both the mono- and the bis-2-hydroxyethyl derivatives when methyl anthranilate was heated with one equivalent of ethylene oxide. The formation of an oxazepine derivative by the action of ethylene oxide on methyl *N*-methylanthranilate was also described by Kiprianov.

The structure of the hydroxyethyloxazepine derivative (II; X = OH) is confirmed by molecular-weight determination, the consumption of one equivalent of alkali on hydrolysis,

* Part XI, *J.*, 1952, 4296.

the formation of a monochloro-derivative (II; X = Cl) on treatment with phosphorus oxychloride, and the production of methyl *NN*-di-2-hydroxyethylanthranilate (IV; X = OH, R = Me) by the action of methanolic hydrogen chloride. The bishydroxyethyl ester (IV; X = OH, R = Me), when treated with phosphorus oxychloride, affords methyl *NN*-di-2-chloroethylanthranilate (IV; X = Cl, R = Me) which may be hydrolysed to the


(II)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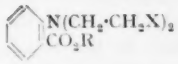
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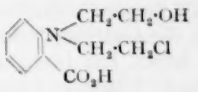
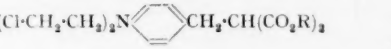
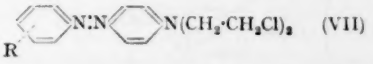

(V)

corresponding acid (IV; X = Cl, R = H). The monohydroxy-ethyl compound (III; X = OH, R = Me) has similarly been converted into the chloro-ester (III; X = Cl, R = Me) and the chloro-acid (III; X = Cl, R = H). Hydrolysis of the chloro-oxazepine derivative (II; X = Cl) with concentrated hydrochloric acid yields *N*-2-chloroethyl-*N*-2-hydroxyethylanthranilic acid (V).

Vigorous acid hydrolysis of the ester (VI; R = Et) resulted in some decarboxylation but under milder conditions it was possible to obtain the hydrochloride of *NN*-di-2-chloroethyl-*p*-aminobenzylmalonic acid (VI; R = H).

(VI) 


(VII)

NN-Di-2-chloroethyl-*p*-aminoazobenzene (VII; R = H), which is an effective inhibitor of the growth of the transplanted Walker rat carcinoma, has been prepared by coupling benzenediazonium chloride with *NN*-di-2-chloroethylaniline in acid solution (Everett and Ross, *loc. cit.*). 4-(*NN*-Di-2″-chloroethylamino)azobenzene-2′-, -3′-, and -4′-carboxylic acids (VII; R = CO_2H) have now been prepared by similarly coupling the appropriate diazotised amino-acid.

A correlation between the chemical reactivity of the aryl-2-halogenoalkylamines and their biological activity has been established (Ross, *loc. cit.*, 1953): in view of this it was of interest to determine the rates of hydrolysis of the new compounds. Table 1 shows the rates for the esters, the free acids, and their sodium salts: the values for the salts were obtained by neutralising the acids with sodium hydroxide, adjusting the acetone concentration to 50%, and then heating in the usual way. In the case of the free acids and the

TABLE 1. *The extent of hydrolysis of 2-chloroethylamino-acids in 50% acetone at 66°. Concn. of amino-acid, 0·02M. Time, 30 min.*

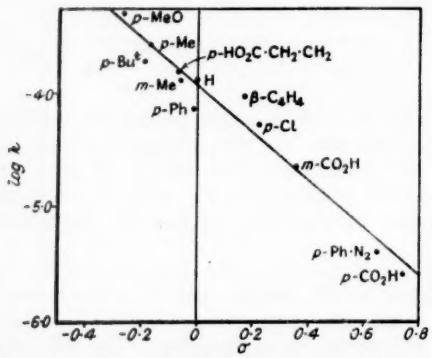
Acid	Free acid, H or Cl (%)	Ester H or Cl (%)	Sodium salt H (%)	Sodium salt Cl (%) (obs.)	Sodium salt Cl (%) (calc.)	pK_a of acid *	Solubility of acid in 4% $COMe_2$ (mg./100 ml.) †
o-$HO_2C{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CH_2Cl)_2$	10	48	41	70	(111)	7·1	—
m-$HO_2C{\cdot}C_6H_4{\cdot}N(CH_2{\cdot}CH_2Cl)_2$	4	4	16	26	30	6·0	9
$HO_2C{\cdot}[CH_2]_n{-}C_6H_4{-}N(CH_2{\cdot}CH_2Cl)_2$ n = 0	1	1	5	12	13	6·6	9
1	17	15	22	39	45	6·1	43
2	24	21	20	41	45	6·4	12
3	32	23	22	42	45	6·5	12
4	27	24	18	38	41	—	5

* Determined in 50% acetone. † Determined by Dr. W. Davis.

esters the amounts of hydrogen and chloride ion liberated are practically identical; the differences in the case of the sodium salts are due to ester formation by reaction of the intermediate carbonium ions with the ionised carboxyl groups (compare Ross, *J.*, 1949, 2589). The experimental values given in Table 1 for the extent of the liberation of chloride ions from the anionic form of the acid are low owing to the production of acid during the

hydrolysis, which reduces the number of carboxyl groups in the ionised form. Since the rate of hydrolysis of the free acid is known it is possible to calculate the true values for the chloride ion liberation—these values represent the actual reactivity of the halogen atom. The validity of the calculation made was shown by hydrolysing the sodium salt of the acid (I; $n = 3$) whilst carefully titrating the solution with sodium hydroxide in 50% acetone. Under these conditions the carboxyl groups will always be ionised and the observed value of 46% for the liberation of chloride ions compares well with the calculated value of 45%. Even the corrected values may be a little low since allowance has not been made for any acid which has been esterified in the reaction. 4-2′-Chloroethyl-2 : 3 : 4 : 7-tetrahydro-7-keto-5 : 6-benz-1 : 4-oxazepine (II; X = Cl) is hydrolysed at the rate of 8% in 30 min. under the standard conditions.

In order to assess the rate of reaction of the acidic chloroethylamines under physiological conditions the rate of elimination of chloride ions at 37° in a solution buffered with sodium hydrogen carbonate was determined. The percentage liberation of chloride ion in one hour was as follows: acid (I; $n = 0$), 10·2; ($n = 1$), 75; ($n = 2$), 77·5; ($n = 3$), 75; and *NN*-di-2-chloroethyl-*m*-aminobenzoic acid, 34. At 20° the phenylacetic acid derivative (I; $n = 1$) is hydrolysed at the rate of 12% in one hour in bicarbonate buffer; this value may be compared with the figure of 60% in one hour at 25° under similar conditions



Graph showing the relationship between log k and σ.

given for *NN*-di-2-chloroethylmethylamine (Golumbic, Fruton, and Bergmann, *J. Org. Chem.*, 1946, **11**, 518).

Hammett has shown that the equation $\log k = \log k_0 + \sigma\rho$ expresses the relation between the rate or equilibrium constants of a general reaction for a series of substituted aromatic compounds, k and k_0 being the constant of the substituted and unsubstituted members respectively, σ a constant for the substituting group, and ρ a constant for the general reaction. If the unimolecular rate constants for the hydrolysis of a series of substituted aryldi-2-chloroethylamines are plotted against the σ values assigned by Hammett ("Physical Organic Chemistry," McGraw Hill Book Co., New York, 1940, p. 188), the graph shown is obtained. In view of the complexity of the hydrolysis reaction involving, as it does, the elimination of two halogen atoms the general agreement between the experimentally determined points and the straight line obtained by the method of least squares is considered satisfactory.

The value of $\log k_0$ calculated from the twelve points is −3·95, in good agreement with the experimental value of −3·91. The value of ρ for the reaction is −2·10. When the hydrolysis constant of the appropriate compound is known the equation $\sigma = \log k - 3{\cdot}95/2{\cdot}10$ enables the σ values for other substituents to be calculated. Table 2 gives some values of σ calculated from rates determined in studies of aryldi-2-chloroethylamines. In two instances the values may be compared with those assigned by Hammett and the agreement is satisfactory.

Biological Results (personal communication from Professor A. Haddow).—All the acids (I) inhibit the growth of transplanted Walker rat carcinoma; moderate activity is shown by the acids ($n = 0$, 2, and 4), and compound ($n = 1$) shows high activity, whilst

(I; $n = 3$) is outstanding. The methyl and ethyl esters of the acids (I) are all active, except the ethyl benzoate derivative ($n = 0$): the corresponding methyl ester shows slight activity, probably because it is more easily hydrolysed to the free acid *in vivo*. *NN*-Di-2-chloroethyl-*m*- and -*o*-aminobenzoic acids and their methyl esters are effective compounds. The monofunctional lactone (II; X = Cl) and chlorohydrin (V) are inactive, thus confirming the greater effectiveness of bifunctional compounds (Goldacre, Loveless, and Ross, *Nature*, 1949, **163**, 667; Loveless and Ross, *ibid.*, 1950, **166**, 1112). Diethyl *NN*-di-2′-chloroethyl-4-aminophthalate and *NN*-di-2′-chloroethyl-4-aminobenzylmalonic acid are inactive.

TABLE 2.

Substituent	Hydrolysis (%) *	log *k* (sec.$^{-1}$)	σ (calc.)	Substituent	Hydrolysis (%) *	log *k* (sec.$^{-1}$)	σ (calc.)
m-CO_2Et	4·5	−4·592	0·306	*p*-$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$	23	−3·838	−0·054
p-Br	6	−4·46	0·244 [a]	*p*-$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	33	−3·653	−0·143
p-$CH_2{\cdot}CO_2Et$	15	−4·044	0·045	*p*-Bu^n	36	−3·606	−0·164
p-$CH_2{\cdot}CO_2H$	17	−3·985	0·017	*p*-NHAc	42	−3·519	−0·205
p-CH:CHPh	18	−3·958	0·004	*p*-OEt	53	−3·38	−0·27 [b]
p-$CH_2{\cdot}CH_2{\cdot}CO_2Et$	21	−3·883	−0·030	*p*-OH	56	−3·317	−0·301

* For conditions see Table 1. [a] Hammett gives 0·231. [b] Hammett gives −0·25.

The especial activity of *NN*-di-2-chloroethyl-γ-*p*-aminophenylbutyric acid cannot be ascribed to exceptional chemical reactivity or physical properties (see Table 1) but appears to be connected with its molecular structure. The pK_a values given in Table 1 were determined in 50% acetone; since the values are probably about 1·5 pH units lower in purely aqueous solutions (Cavill, Gibson, and Nyholm, *J.*, 1949, 2466), all the acids are practically wholly dissociated under physiological conditions. It is interesting that outstandingly high trypanocidal activity was demonstrated in the phenylbutyric acid derivative in a series of arsenoso-compounds of structure (VIII) (Eagle, *Science*, 1945, **101**, 69).

(VIII) $CO_2H{\cdot}[CH_2]_n$—C$_6$H$_3$—As→O

p-Butyl-*NN*-di-2-chloroethylaniline is a moderately active inhibitor, not being as effective as the acidic derivatives, and of the three azo-compounds (VII) only the 2′-carboxylic acid is active.

EXPERIMENTAL

NN-*Di-2-chloroethyl*-p-*aminophenylacetic Acid.*—Ethyl *p*-aminophenylacetate (18 g.), ethylene oxide (12 ml.), and benzene (10 ml.) were heated at 150° for 14 hr. The resulting *ethyl* NN-*di-2-hydroxyethyl*-p-*aminophenylacetate* formed stout prisms, m. p. 70·5—71·5°, from benzene–light petroleum (b. p. 40—60°) (Found: C, 63·1; H, 8·0. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9%). A solution of the hydroxyethyl ester (15 g.) in benzene (40 ml.) containing phosphorus oxychloride (15 ml.) was heated for 1 hr., the two layers becoming homogeneous. The solution was poured on ice, the benzene layer dried (Na_2SO_4), shaken with activated alumina, and evaporated, affording *ethyl* NN-*di-2-chloroethyl*-p-*aminophenylacetate*, prismatic needles, m. p. 52—53°, from pentane (Found: C, 54·8; H, 6·5. $C_{14}H_{19}O_2NCl_2$ requires C, 55·3; H, 6·3%). When the ester was heated with five times its weight of concentrated hydrochloric acid the *chloroethyl-acid* was obtained. It formed fine needles, m. p. 105°, from benzene–pentane (Found: C, 52·0; H, 5·7. $C_{12}H_{15}O_2NCl_2$ requires C, 52·2; H, 5·5%).

NN-*Di-2-chloroethyl*-p-*aminophenylpropionic Acid.*—*Ethyl* NN-*di-2-hydroxyethyl*-p-*aminophenylpropionate*, prepared from ethyl *p*-aminophenylpropionate as described above, was an oil, b. p. 160—170°/1 mm. (Found: C, 64·0; H, 8·6. $C_{15}H_{23}O_4N$ requires C, 64·0; H, 8·2%). It was similarly converted into the *di-2-chloroethyl* ester, which formed oblong plates, m. p. 40·5°, from light petroleum (b. p. 40—60°) (Found: C, 56·3, 56·9; H, 6·7, 6·5. $C_{15}H_{21}O_2NCl_2$ requires C, 56·6; H, 6·7%) and into the *acid*, which crystallised from benzene–light petroleum (b. p. 40—60°) as fine needles, m. p. 114—115° (Found: C, 53·7; H, 6·2. $C_{13}H_{17}O_2NCl_2$ requires C, 53·8; H, 5·9%).

Nitration of γ-Phenylbutyric Acid.—(*a*) γ-Phenylbutyric acid (Truce and Olsen, *J. Amer. Chem. Soc.*, 1952, **74**, 4721) (59 g.) was added to a well-stirred mixture of concentrated nitric acid (118

ml.) and concentrated sulphuric acid (118 ml.) at −5° during 1½ hr. The mixture was allowed to reach room temperature (2 hr.), then poured on ice and filtered. The *dinitro-acid* crystallised from *iso*propyl ether as prisms, m. p. 97—98° (Found : C, 47·3; H, 4·0%; equiv., 256. $C_{10}H_{10}O_6N_2$ requires C, 47·2; H, 4·0%; equiv., 254).

(*b*) The crude nitration product obtained by the method of van der Scheer (*ibid.*, 1934, **56**, 744) had an equivalent weight of 209. After several crystallisations from *iso*propyl ether γ-*p*-nitrophenylbutyric acid, m. p. 92°, was obtained (van der Scheer gives m. p. 92—93°).

Methyl p-*Aminophenylbutyrate.*—Acetyl chloride (3 ml.) was cautiously added to a solution of the nitro-acid (18 g.) in methanol (50 ml.) and the solution was heated under reflux for 1 hr. After the addition of acetyl chloride (3 ml.) to the cooled solution heating was continued for a further 2 hr. and then one-half of the solvent was removed by distillation. The residue was diluted with water and extracted with ether. After washing of the extract with 2N-sodium carbonate evaporation gave *methyl* γ-p-*nitrophenylbutyrate*, m. p. 39—41°, rhombs from light petroleum (b. p. 40—60°) or prismatic needles from methanol (Found : C, 59·3; H, 5·8. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9%). A solution of the nitro-ester (18 g.) in methanol (100 ml.) containing palladium–calcium carbonate (2 g.; 2%) was shaken in hydrogen, the theoretical volume of hydrogen for the reduction of the nitro-group being rapidly taken up. Evaporation of the filtered solution gave an oil which crystallised from light petroleum (b. p. 40—60°). *Methyl* p-*aminophenylbutyrate* formed needles, m. p. 42° (Found : C, 68·7; H, 7·7. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8%).

NN-*Di*-2-*chloroethyl*-γ-p-*aminophenylbutyric Acid.*—(*a*) The amino-ester may be converted into the di-2-chloroethyl-acid as described above, but the following method gave higher yields.

(*b*) Ethylene oxide (25 ml.) was added to a stirred suspension of the amino-ester (10 g.) in N-acetic acid (50 ml.). After 4 hr. the solution became homogeneous and the excess of ethylene oxide was removed under reduced pressure. The oily hydroxyethyl compound which separated was extracted with ether and washed with 2N-sodium carbonate. The residue obtained after evaporation of the dried solution was dissolved in benzene (150 ml.), and the remaining water was removed by distilling off 50 ml. of solvent. After addition of phosphorus oxychloride (15 ml.) the mixture was heated under reflux for 1 hr. The solvent and excess of oxychloride were then removed under reduced pressure and the residue heated for 1 hr. with concentrated hydrochloric acid (40 ml.). The cooled solution was diluted with water (200 ml.) and extracted with ether (4 × 150 ml.). Evaporation of these extracts gave NN-*di*-2-*chloroethyl*-γ-p-*aminophenylbutyric acid* which formed flattened needles, m. p. 64—66°, from light petroleum (b. p. 40—60°) (Found : C, 55·5; H, 6·1. $C_{14}H_{19}O_2NCl_2$ requires C, 55·3; H, 6·3%).

NN-*Di*-2-*chloro*-n-*propyl*-γ-p-*aminophenylbutyric Acid.*—A mixture of the *p*-aminophenylbutyric ester (5 g.), propylene oxide (12·5 ml.), and N-acetic acid (25 ml.) was stirred for 7 hr. and then heated under reflux for 1 hr.; two clear layers were formed. The hydroxypropyl compound was isolated as an oil which was converted into the chloride as above. The non-crystalline chloroethyl ester was hydrolysed with concentrated hydrochloric acid. NN-*Di*-2-*chloropropyl*-γ-p-*aminophenylbutyric acid* formed prisms (from pentane), m. p. 67—69° (Found : C, 58·2; H, 7·1%; equiv., 330. $C_{16}H_{23}O_2NCl_2$ requires C, 57·9; H, 7·0%; equiv., 332).

p-n-*Butyl*-NN-*di*-2-*chloroethylaniline.*—*p*-*n*-Butylaniline was treated with ethylene oxide in benzene in the usual manner. The *di*-2-*hydroxyethyl* derivative formed plates, m. p. 52°, from light petroleum (b. p. 60—80°) (Found : C, 70·8; H, 9·9. $C_{14}H_{23}O_2N$ requires C, 70·8; H, 9·8%); it formed a *picrate*, m. p. 67°, yellow plates from benzene (Found : C, 51·1; H, 5·9; N, 12·1. $C_{20}H_{26}O_9N_4$ requires C, 51·5; H, 5·6; N, 12·0%). Phosphorus oxychloride converted the hydroxy-compound into the *di*-2-*chloroethyl* derivative, an oil, b. p. 180°/4 mm., 155—160°/1 mm. (Found : Cl, 25·5. $C_{14}H_{21}NCl_2$ requires Cl, 25·8%).

NN-*Di*-2-*chloroethyl*-δ-p-*aminophenylvaleric Acid.*—Cinnamylidenemalonic acid (Liebermann, *Ber.*, 1895, **28**, 1439) was decarboxylated by heat in pyridine, and the product was reduced in ethanol at a platinum catalyst. The phenylvaleric acid was nitrated by Freedman and Doak's method (*J. Amer. Chem. Soc.*, 1949, **71**, 779), giving the nitro-acid (45%), m. p. 83°. Esterification and reduction, as described for nitrophenylbutyric acid, gave the amino-ester, characterised by hydrolysis to the known δ-*p*-aminophenylvaleric acid, m. p. 111—113°. The amino-ester was converted directly into the chloroethyl acid in the usual manner. NN-*Di*-2-*chloroethyl*-δ-p-*aminophenylvaleric acid* formed prismatic needles, m. p. 87°, from light petroleum (b. p. 60—80°) (Found : C, 56·7; H, 6·1; Cl, 22·4%; equiv., 318. $C_{15}H_{21}O_2NCl_2$ requires C, 56·6; H, 6·6; Cl, 22·3%; equiv., 318).

NN-*Di*-2-*chloroethyl*-m-*aminobenzoic Acid.*—By heating with ethylene oxide in benzene solution and then treatment with phosphorus oxychloride, methyl *m*-aminobenzoate was converted

into *methyl* NN-*di*-2-*chloroethyl*-m-*aminobenzoate*, m. p. 61—62°, thick rectangular plates from light petroleum (b. p. 60—80°) (Found: C, 52·4; H, 5·7. $C_{12}H_{15}O_2NCl_2$ requires C, 52·2; H, 5·5%). Hydrolysis with concentrated hydrochloric acid afforded the *chloroethyl-acid*, m. p. 177—178°, flattened needles from benzene (Found: C, 50·3; H, 5·1%; equiv., 265. $C_{11}H_{13}O_2NCl_2$ requires C, 50·4; H, 5·0%; equiv., 262).

Diethyl NN-*Di*-2′-*chloroethyl*-4-*aminophthalate*.—The non-crystalline product (18 g.) obtained by heating diethyl 4-aminophthalate with ethylene oxide in benzene was heated for ½ hr. with thionyl chloride (12 ml.) in benzene (75 ml.). The mixture was poured on ice, and the benzene layer washed with 2N-sodium carbonate and evaporated. A solution of the residue in light petroleum (b. p. 60—80°) was passed down a column of activated alumina. Further elution of the column with light petroleum did not remove any material but washing with *cyclo*hexane gave *diethyl* NN-*di*-2′-*chloroethyl*-4-*aminophthalate*, which formed fine needles, m. p. 82—83°, from light petroleum (b. p. 40—60°) (Found: C, 53·3; H, 6·1. $C_{16}H_{21}O_4NCl_2$ requires C, 53·1; H, 5·9%). When the diester (1 g.) was heated under reflux for 2 hr. with concentrated hydrochloric acid (20 ml.) *NN*-di-2-chloroethyl-*m*-aminobenzoic acid, m. p. 177° not depressed by admixture with a specimen prepared as above, was produced (Found: C, 50·8; H, 4·7%; equiv., 264).

Action of Ethylene Oxide on Methyl Anthranilate.—(*a*) Methyl anthranilate (15·1 g.), ethylene oxide (10 ml.), and benzene (10 ml.) were heated at 150° for 16 hr. The residue obtained after the evaporation of the solvent was crystallised from benzene–light petroleum (b. p. 60—80°). 2 : 3 : 4 : 7-*Tetrahydro*-4-2′-*hydroxyethyl*-7-*keto*-4 : 6-*benz*-1 : 4-*oxazepine* formed plates, m. p. 80° [Found: C, 63·8; H, 6·5%; equiv., 206; *M* (Rast), 200. $C_{11}H_{13}O_3N$ requires C, 63·8; H, 6·3%; equiv. and *M*, 207]. In one run the main product was *methyl* N-2-*hydroxyethylanthranilate*, m. p. 70°, platelets from light petroleum (b. p. 40—60°) (Found: C, 61·6; H, 6·8. Calc. for $C_{10}H_{13}O_3N$: C, 61·3; H, 6·7; N, 7·2%).

(*b*) When methyl anthranilate was treated for 24 hr. at 20° with an excess of ethylene oxide in N-acetic acid the monohydroxyethyl derivative, m. p. 71—72°, long needles from light petroleum (b. p. 40—60°) (Found: C, 61·6; H, 6·8; N, 7·2%), was the only product. It formed a *hydrochloride*, m. p. 162—164°, hard prisms from methanol–ether (Found: C, 51·5; H, 6·2; N, 6·3; Cl, 15·2. $C_{10}H_{14}O_3NCl$ requires C, 51·8; H, 6·1; N, 6·0; Cl, 15·3%). Kiprianov (*loc. cit.*) described a monohydroxyethyl derivative, m. p. 70·5—71·5°, which gave a hydrochloride, m. p. 100°.

N-2-*Chloroethyl*-N-2-*hydroxyethylanthranilic Acid*.—The tetrahydrohydroxyoxazepine (5 g.), phosphorus oxychloride (20 ml.), and benzene (200 ml.) were heated under reflux for ½ hr. The benzene layer was poured on ice, and the tarry residue was treated with cold saturated sodium hydrogen carbonate solution and then extracted with benzene. The combined benzene extracts were dried and evaporated, and the residue was passed in light petroleum (b. p. 60—80°) down a column of activated alumina. The early eluates afforded 4-2′-*chloroethyl*-2 : 3 : 4 : 7-*tetrahydro*-7-*keto*-5 : 6-*benz*-1 : 4-*oxazepine*, m. p. 55°, plates from *cyclo*hexane [Found: C, 59·1; H, 5·6; Cl, 15·7%; *M* (Rast), 200. $C_{11}H_{12}O_2NCl$ requires C, 58·5; H, 5·4; Cl, 15·7%; *M*, 225·7]. When hydrolysed by hot concentrated hydrochloric acid the oxazepine yielded N-2-*chloroethyl*-N-2-*hydroxyethylanthranilic acid*, m. p. 80°, prisms from ether (Found: C, 54·5; H, 5·7; Cl, 14·6%; equiv., 241. $C_{11}H_{14}O_3NCl$ requires C, 54·2; H, 5·8; Cl, 14·6%; equiv., 243·7). The non-crystalline ester, formed by the action of ethereal diazomethane on the acid, gave a *picrate*, m. p. 132—133°, prisms from methanol (Found: C, 44·7; H, 4·1. $C_{18}H_{19}O_{10}N_4Cl$ requires C, 44·4; H, 3·9%).

NN-*Di*-2-*chloroethylanthranilic Acid*.—A solution of the tetrahydrohydroxyethyloxazepine (3 g.) in methanol (50 ml.) was saturated with dry hydrogen chloride at 0°. After ½ hr. under reflux the solution was cooled, resaturated with hydrogen chloride, and heated for a further ½ hr. The residue, obtained after removal of the methanol by distillation, solidified and was crystallised from acetone–methanol. The *hydrochloride* of methyl *NN*-di-2-hydroxyethylanthranilate formed plates, m. p. 137—138° (decomp.) (Found: C, 52·1; H, 6·7. $C_{12}H_{15}O_4NCl$ requires C, 52·3; H, 6·6%). Kiprianov (*loc. cit.*) records m. p. 160° for a compound claimed to be this hydrochloride. The ester formed a *picrate*, m. p. 133°, prisms from ethanol (Found: C, 46·1; H, 4·5. $C_{18}H_{20}O_{11}N_4$ requires C, 46·1; H, 4·3%). The hydrochloride (1 g.) and phosphorus oxychloride (4 ml.) were heated under reflux for ½ hr., cooled, and poured on ice. Sodium acetate was added and the mixture extracted with benzene. The benzene extract yielded methyl *NN*-di-2-chloroethylanthranilate as an oil which formed a *picrate*, m. p. 103°, plates from methanol (Found: C, 43·2; H, 3·9. $C_{18}H_{18}O_9N_4Cl_2$ requires C, 42·8; H, 3·6%). When the ester was heated with concentrated hydrochloric acid NN-*di*-2-*chloroethylanthranilic acid*,

m. p. 85°, needles from benzene–light petroleum (b. p. 60—80°) (Found: C, 50·6; H, 5·4. $C_{11}H_{13}O_2NCl_2$ requires C, 50·4; H, 5·0%), was obtained.

N-2-*Chloroethylanthranilic Acid.*—Treatment of methyl *N*-2-hydroxyethylanthranilate with phosphorus oxychloride in the usual manner gave *methyl* N-2-*chloroethylanthranilate*, m. p. 35°, platelets from pentane (Found: C, 55·9; H, 5·7. $C_{10}H_{12}O_2NCl$ requires C, 56·2; H, 5·7%). On hydrolysis the corresponding *acid*, m. p. 115—116°, platelets from light petroleum (b. p. 60—80°) (Found: C, 54·7; H, 5·3. $C_9H_{10}O_2NCl$ requires C, 54·2; H, 5·1), was obtained.

NN-*Di*-2′-*chloroethyl*-4-*aminobenzylmalonic Acid.*—Condensation of diethyl sodiomalonate with *p*-nitrobenzyl chloride gave a product, m. p. 166°, which is a bisnitrobenzyl derivative and not the required mononitro-compound (the m. p. 168·5° given in Heilbron's " Dictionary of Organic Compounds " for *p*-nitrobenzylmalonic ester is incorrect). The required mononitrobenzyl derivative was prepared by nitrating diethyl benzylmalonate; it formed prisms, m. p. 60° from benzene (lit., m. p. 63°). The amino-ester (m. p. 60°; lit., 64°), obtained by catalytic (palladium–calcium carbonate in ethanol) reduction was treated with ethylene oxide in N-acetic acid as described above. After 24 hr. the non-crystalline product was isolated and treated with phosphorus oxychloride in benzene. The chloro-compound was submitted to a chromatographic purification but did not crystallise.

When the chloro-ester (750 mg.) was heated under reflux for ½ hr. with concentrated hydrochloric acid (2 ml.) the product obtained formed needles, m. p. 112° (from benzene) alone or mixed with *NN*-di-2-chloroethyl-*p*-aminophenylpropionic acid (m. p. 114°).

Evaporating a solution of the chloro-ester (3 g.) in concentrated hydrochloric acid (15 ml.) on a steam-bath until no further reduction in bulk occurred, and cooling, gave a pasty solid. This was collected, washed with a little ice-cold hydrochloric acid, and crystallised from ethyl acetate, affording the *hydrochloride* of *NN*-di-2-chloroethyl-*p*-aminobenzylmalonic acid as small prisms, m. p. 163° (decomp.) (Found: C, 45·5; H, 5·2%; equiv., 126. $C_{14}H_{18}O_4NCl_3$ requires C, 45·4; H, 4·9%; equiv., 123·5). The free acid did not crystallise.

4-(NN-*Di*-2″-*chloroethylamino*)*azobenzenecarboxylic Acids.*—The diazonium salt prepared by adding sodium nitrite (1·4 g.) in water (10 ml.) to a solution of *p*-aminobenzoic acid (2·8 g.) in water (40 ml.) containing concentrated hydrochloric acid (6 ml.) was added to a solution of *NN*-di-2-chloroethylaniline (4·4 g.) in ethanol (150 ml.). After ½ hr. at room temperature the red precipitate was collected and crystallised from 2-methoxyethanol. 4-(NN-*Di*-2″-*chloroethylamino*)*azobenzene*-4′-*carboxylic acid* formed small orange-red plates, m. p. 212—214° (Found: C, 56·2; H, 5·1; N, 11·1, 11·6. $C_{17}H_{17}O_2N_3Cl_2$ requires C, 55·8; H, 4·7; N, 11·5%).

The 3′-*carboxylic acid*, deep yellow flattened needles (from methanol), m. p. 162—164° (Found: C, 55·9; H, 4·9; N, 11·7%), and the 2′-*carboxylic acid*, deep orange-red plates (from acetone), m. p. 179—180° (Found: C, 56·1; H, 5·0; N, 11·5%), were similarly prepared.

Rate of Hydrolysis of Chloroethylamino-acids in Bicarbonate Solution.—Since the acids dissolved only with difficulty in N/6(" isotonic ")-sodium hydrogen carbonate, even when finely divided, they were dissolved in N/6-sodium hydroxide and this solution was saturated with carbon dioxide, phenolphthalein being used as indicator. Nitrogen was passed through to remove the excess of carbon dioxide—unless this was done precipitation of the acid occurred—and the solution was kept at the required temperature, after which the liberated chloride ion was titrated with silver nitrate (potassium chromate).

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487. *Anodic Syntheses. Part IX.* Unsaturated and Hydroxy-acids. A Direct Stereochemical Connection of Oleic and Elaidic with Erucic and Brassidic Acids.*

By D. G. Bounds, R. P. Linstead, and B. C. L. Weedon.

Undec-10-enoic, oleic, elaidic, and *threo-* and *erythro*-9 : 10-dihydroxystearic acids undergo the Kolbe reaction to give the expected products in 20—50% yields. Anodic cross-coupling of these acids with adipic half-ester occurs readily, and illustrates a convenient method for the synthesis of unsaturated long-chain fatty acids and their dihydroxy-derivatives.

The success of anodic methods in the synthesis of many saturated fatty acids with both straight and branched chains prompted an examination of similar routes for the preparation of unsaturated acids. Interest in these compounds has been enhanced in recent years by reports that a number of them are growth factors † for various micro-organisms (cf. Pollock, *Nature*, 1948, **161**, 853; Boughton and Pollock, *Biochem. J.*, 1953, **52**, 261), and by the realisation that lipids from tubercle bacilli contain unsaturated branched-chain fatty acids (Polgar and Robinson, *Chem. and Ind.*, 1951, 685; Cason and Sumrell, *J. Biol. Chem.*, 1951, **192**, 405; Cason, Freeman, and Sumrell, *ibid.*, p. 415). Both for biological testing, and for confirmation of the structures provisionally assigned to some of the natural materials, synthetic acids are required of high purity and of known configuration. This paper describes anodic syntheses of erucic and brassidic (*cis-* and *trans*-docos-13-enoic) acids. Erucic acid occurs in the seed fats of the Cruciferæ and Tropæolacæ, and, together with brassidic acid, has been synthesised by Bowman (*J.*, 1950, 177).

By comparison with the anodic reactions of saturated fatty acids, those of unsaturated acids have received little study; and much of the earlier work was carried out under conditions which would not now be regarded as the most suitable for coupling reactions of the Kolbe type. However, previous investigations indicate that normal coupling occurs on electrolysis of olefinic acids provided that the double bond is separated from the carboxyl to be eliminated by at least two carbon atoms (see a summary by Weedon, *Quart. Reviews*, 1952, **6**, 300). Thus hex-4-enoic (Fichter and Holbro, *Helv. Chim. Acta*, 1937, **20**, 333), undec-10-enoic (I*a*), oleic (I*b*) (Petersen, *Z. Elektrochem.*, 1912, **18**, 711), petroselenic (octadeca-*cis*-6-enoic) and erucic acids (Ueno and Tamura, *J. Soc. Chem. Ind., Japan*, 1943, **46**, 1213) are reported to undergo anodic coupling, though the geometrical configurations of the products have not been determined, and "crossed" coupling reactions of oct-7-enoic (Ruzicka, Stoll, and Schinz, *Helv. Chim. Acta*, 1928, **11**, 670) and undec-10-enoic acids (Ruzicka, Stoll, Scherrer, Schinz, and Seidel, *ibid.*, 1932, **15**, 1459; Gustbée and Stenhagen, *Sartryck ur Svensk Kemisk Tidskr.*, 1942, **54**, 243) with half-esters have been used to yield terminally unsaturated acids. Since few details are available of a number of these reactions, some of them have been repeated in the present studies.

Electrolysis of undec-10-enoic acid, and of a mixture of the latter with methyl hydrogen adipate (cf. Ruzicka *et al.*, *loc. cit.*, 1932), led to the hydrocarbon (II*a*) and pentadec-14-enoic acid (III*a*) in 43 and 22% yield respectively. The structure of (III*a*) was confirmed by ozonolysis to tetradecanedioic acid.

Electrolysis of oleic acid gave (23%) the crystalline tetratriacontadiene (II*b*) reported by Petersen (*loc. cit.*), whilst elaidic acid under the same conditions yielded (44%) a previously unknown, higher-melting, isomeric hydrocarbon. That no double bond migration had occurred in either reaction was shown by oxidative degradation of the two dienes (see below). It was therefore concluded that the configurations of the double bonds had been preserved during the electrolyses.

When oleic and elaidic acids were electrolysed in the presence of an excess of methyl

* Part VIII, *J.*, 1953, 1538.

† The claim (Boer, Jansen, and Kentie, *Nature*, 1946, **158**, 201) that "vaccenic acid" promotes the growth of rats has not been confirmed in later investigations (cf. Gupta, Hilditch, Paul, and Shrivastava, *J.*, 1950, 3484).

hydrogen adipate the expected mixtures of three products were obtained by both symmetrical and unsymmetrical coupling of the two components. By distillation, and subsequent hydrolysis of the unsymmetrical products, erucic (*cis*-III*b*) and brassidic acid (*trans*-III*b*) respectively were obtained in *ca.* 30% overall yield.

$$\underset{\text{(I)}}{CHR{:}CH{\cdot}[CH_2]_n{\cdot}CO_2H} + HO_2C{\cdot}[CH_2]_4{\cdot}CO_2Me \longrightarrow$$

$$\underset{\text{(II)}}{CHR{:}CH{\cdot}[CH_2]_{24}{\cdot}CH{:}CHR} + MeO_2C{\cdot}[CH_2]_6{\cdot}CO_2Me + CHR{:}CH{\cdot}[CH_2]_{n+4}{\cdot}CO_2Me \downarrow$$

$$\underset{\text{(III)}}{CHR{:}CH{\cdot}[CH_2]_{n+4}{\cdot}CO_2H}$$

[*a*, R = H, $n = 8$; *b*, R = $Me{\cdot}[CH_2]_7{\cdot}$, $n = 7$]

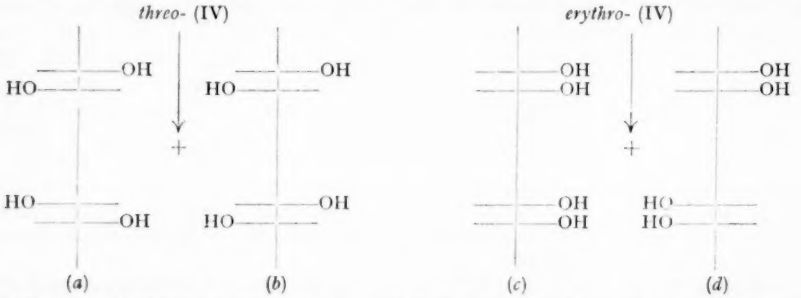
Since *cis*- and *trans*-unsaturated fatty acids may be prepared from the corresponding saturated *erythro*- and *threo*-glycols (Ruzicka, Plattner, and Widner, *Helv. Chim. Acta*, 1942, **25**, 604, 1086; Baudart, *Bull. Soc. chim.*, 1946, **13**, 87; Ames and Bowman, *J.*, 1951, 1079) electrolyses of the 9 : 10-dihydroxystearic acids (IV) have also been examined.

$$\underset{\text{(IV)}}{Me{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}CO_2H} + HO_2C{\cdot}[CH_2]_4{\cdot}CO_2Me \longrightarrow$$

$$Me{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_{14}{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_7{\cdot}Me + \underset{\text{(V)}}{}$$

$$MeO_2C{\cdot}[CH_2]_6{\cdot}CO_2Me + Me{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_{11}{\cdot}CO_2Me \longrightarrow \underset{\text{(VI)}}{Me{\cdot}[CH_2]_7{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_{11}{\cdot}CO_2H} \longrightarrow (III\textit{b})$$

These intermediates are more easily purified than oleic and elaidic acids, from which they are readily derived. Previously it has been claimed that both ricinoleic (Lübbe, D.R.-P. **624**, 331; Kitaura, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1937, **16**, 765) and (±)-*threo*-9 : 10-dihydroxystearic acid (Lübbe, *loc. cit.*), unlike α-hydroxy-acids (von Miller and Hofer, *Ber.*, 1894, **27**, 461), undergo the Kolbe reaction. It has now been shown that electrolyses of the (±)-*threo*- and (±)-*erythro*-forms of (IV) give, in 50 and 20% yields, different diastereoisomers of the tetrol (V). From each of these coupling reactions a mixture of two tetrols would be expected; a (±)-compound formed by symmetrical coupling of the enantiomorphs of *threo*- or *erythro*-(IV), and a *meso*-compound formed by crossed coupling.



[For simplicity each of the (±)-tetrols is represented by only one of its enantiomorphs, (*b*) and (*d*).]

These are shown diagrammatically above by projection formulæ (*a*—*d*) of the Fischer type (cf. Hudson, *Adv. Carbohydrate Chem.*, 1948, **3**, 1). Nevertheless in each experiment only one, apparently homogeneous, solid product was isolated. That each solid must, however, be regarded as a mixture of the appropriate pair of isomers was shown in the following manner. Hydroxylation with performic acid (cf. Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504) of the dienes (II*b*) from oleic and elaidic acids gave (70%) the same solid tetrols as were obtained from electrolyses of (±)-*threo*- and (±)-*erythro*-dihydroxystearic acid respectively. In these hydroxylation experiments equimolar

mixtures of two tetrols [(±)- and *meso*] would, of course, be formed by *trans*-addition to the double bonds (cf. Swern, *Chem. Reviews*, 1949, **45**, 1). The possibility (conceivable with the anodic reactions) that only one of the two isomers had been isolated can be ruled out, as the yield is over 50%. The structures of the tetrols were confirmed by oxidative degradation of the mixtures to nonanoic and thapsic acids.

Crossing reactions of *threo*- and *erythro*-dihydroxystearic acids with methyl hydrogen adipate took place normally and, after hydrolysis of the initial products, *threo*- and *erythro*-dihydroxybehenic acids (VI) were isolated (in *ca.* 30% overall yield). These were converted into brassidic and erucic acid respectively by standard procedures (cf. Ames and Bowman, *loc. cit.*) (in 30 and 43% yields based on dihydroxybehenic acid).

It will be apparent that chain extension of an unsaturated fatty acid *via* the dihydroxy-derivative possesses, in general, no merit over the simpler, and more direct, cross-coupling of the parent unsaturated acid; only where the latter is difficult to purify is the alternative process likely to prove superior.

By comparison with the other main routes to long-chain unsaturated fatty acids (*viz.*, the α-methoxy-ketone route, the acyloin route, and the acetylenic route, cf. *Ann. Reports*, 1949—1951) the anodic procedures possess features which may, in some syntheses, afford distinct advantages: (i) By suitable choice of starting materials a product is obtained which is not contaminated by other monocarboxylic acids of approximately the same molecular weight: the required acid is therefore easily purified. (ii) No laborious separation of the *cis*- and the *trans*-form of the product, or of the *erythro*- and the *threo*-form of its dihydroxy-derivative, is involved. (iii) In the preparation of a *trans*-acid, "elaidinisation" of the *cis*-isomer, with consequent risk of partial migration of the double bond, is avoided. (iv) The geometrical configuration of the product is related to that of the starting material. Thus the configurations long accepted for erucic and brassidic acid (Mascarelli, *Atti R. Accad. Lincei*, 1917, **26**, 71) receive additional support from the partial syntheses of these compounds from oleic and elaidic acids.

Experimental

M. p.s are corrected, unless stated otherwise. Those below 35° were determined after solidification of the molten substance in a capillary tube.

Except in the electrolysis of undec-10-enoic acid, no allowance has been made for recovered starting material in calculating yields. Yields of unsymmetrical products are based on the mono-acid used in the electrolysis.

Intermediates.—Undec-10-enoic acid. Commercial undecenoic acid was distilled and the fraction, b. p. 155—157°/10 mm., m. p. 24·5—25·0°, was collected.

Oleic acid. Purification (cf. Smith, *J.*, 1939, 975) of commercial oleic acid, m. p. *ca.* 2°, gave a product, m. p. 12°, $n_D^{18\cdot5}$ 1·4601 (*idem, loc. cit.*, gives m. p. 13·4°, n_D^{20} 1·4597) [Hydrogen no. (cf. Ogg and Cooper, *Analyt. Chem.*, 1949, **21**, 1400), 287. Calc. for 1 double bond, 283].

Elaidic acid. (*a*) Commercial oleic acid was treated with nitrous fumes (cf. Griffiths and Hilditch, *J.*, 1932, 2321). The product, in boiling alcohol, was neutralised with aqueous lithium hydroxide. The lithium salt, which separated on cooling, was collected and fractionally crystallised from 60% aqueous alcohol, giving a solid, m. p. 213—218° (uncorr., sealed capillary), unchanged by further crystallisation. Regeneration of the acid, and one crystallisation from alcohol at 0°, gave elaidic acid, m. p. 42—43° (Mayer, *Annalen*, 1840, **35**, 174, gives m. p. 44—45°).

(*b*) (cf. conversion of *erythro*-9 : 10-dihydroxystearic acid into oleic acid; Ames and Bowman, *J.*, 1951, 1054). Bromination of *threo*-9 : 10-dihydroxystearic acid (140 g.), m. p. 93°, and esterification of the product (150 g.), m. p. 20—23° [from methanol at −50° (charcoal)], gave ethyl *erythro*-9 : 10-dibromostearate (150 g.), a small sample of which was distilled and had b. p. 147—150° (bath-temp.)/10^{-4} mm., n_D^{20} 1·4859 (Found: C, 50·85; H, 8·1. Calc. for $C_{20}H_{38}O_2Br_2$: C, 51·05; H, 8·15%). Debromination of the dibromo-ester in alcohol with zinc gave ethyl elaidate (92 g.), b. p. 185—187°/0·1 mm., n_D^{21} 1·4497. Hydrolysis yielded elaidic acid (80 g., 64% overall yield), m. p. 43—44°, raised by one crystallisation from 80% aqueous alcohol to 44·0—44·3°, n_D^{50} 1·4477 (Szalágyi, *Biochem. Z.*, 1914, **66**, 152, gives n_D^{45} 1·4499).

9 : 10-*Dihydroxystearic acid.* The *threo*-form, m. p. 93°, was prepared from commercial oleic acid and performic acid (cf. Swern, Billen, Findlay, and Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**,

1786), and the *erythro*-form, m. p. 131°, by oxidation of sodium oleate with alkaline permanganate (cf. Le Sueur, *J.*, 1901, 1315).

Methyl hydrogen adipate. The half ester was prepared from adipic acid and methyl adipate (cf. Swann, Oehler, and Buswell, *Org. Synth.*, Coll. Vol. II, p. 276).

Apparatus.—Three cells, "A"—"C," were used. These consisted of cylindrical glass vessels containing two parallel platinum plates, placed *ca.* 3 mm. apart, as electrodes. In cell "A" the electrodes measured 2 × 2·5 cm., in cell "B" 3·5 × 2·5 cm., and in cell "C" 6·5 × 5 cm. Cell "C" (14 × 3") was fitted with two spiral cooling-coils (10 × 1") through which cold water was passed.

Electrolyses.—These were carried out with commercial absolute methanol as solvent, to which sufficient sodium had been added to neutralise *ca.* 2% of the total acids used. During the electrolyses the cells were cooled in an ice-bath (internal temperature of cells <50°), and the direction of the current was reversed periodically. At intervals in the symmetrical coupling reactions, and towards the end of the unsymmetrical coupling reactions, it was necessary to interrupt the experiments and remove polymeric deposits from the electrodes. Electrolyses were continued until the electrolyte became slightly alkaline. Before isolation of the products, the cell contents were acidified with either dilute sulphuric acid or glacial acetic acid.

Hydrolyses.—Unsaturated esters were hydrolysed, in an atmosphere of nitrogen, by being vigorously stirred under reflux for 2 hr. with a 2N-solution of sodium hydroxide (2 mols.) in methanol–water (4 : 1).

Eicosa-1 : 19-*diene* [with R. W. KIERSTEAD].—A solution of sodium undec-10-enoate (from 12·0 g. of undec-10-enoic acid and 1·5 g. of sodium) in methanol (60 c.c.) was electrolysed in cell "B." During the reaction the electrolyte was kept slightly acidic by the slow addition of undec-10-enoic acid (12·0 g.) in methanol (20 c.c.) (current, 0·5—0·6 amp.). After the electrolysis, the cell contents were acidified and the products were extracted with ether and separated in the usual way into neutral and acidic fractions. From the latter undec-10-enoic acid (8·3 g.) was recovered. Distillation of the neutral fraction gave eicosa-1 : 19-diene (5·0 g., 43%, based on unrecovered starting material), b. p. 125—130°/0·2 mm., n_D^{24} 1·4511, m. p. 17—19°, raised to 19·5—20° (uncorr.) by crystallisation from alcohol (Petersen, *Z. Electrochem.*, 1912, **18**, 710, gives m. p. 20·3°).

Pentadec-14-*enoic Acid* (cf. Ruzicka, Stoll, Schinz, and Seidel, *Helv. Chim. Acta*, 1932, **15**, 1459).—A solution of methyl hydrogen adipate (8·0 g.; 0·05 mol.) in methanol (65 c.c.) was electrolysed in cell "B." During the reaction methyl hydrogen adipate (60 g., 0·39 mol.) and undec-10-enoic acid (24 g., 0·13 mol.) in methanol (40 c.c.) were added slowly, the electrolyte thus being kept slightly acidic (current, 0·5 amp.; faradays passed, *ca.* 1·2 times theoretical, calculated on the basis of the total amount of acids used). After the electrolysis, the cell contents were acidified and evaporated. The residue was extracted with ether, and the extract was washed with aqueous sodium hydroxide (2% w/v), dried, and evaporated. The residue was hydrolysed and the product separated into acidic and neutral fractions. The latter yielded eicosa-1 : 19-diene (1·7 g., 5%), m. p. 18·5—20·0°. The acidic fraction was extracted with light petroleum (b. p. 60—80°; 3 × 70 c.c.), and the extract was evaporated. Four crystallisations of the residue (6·8 g., 22%), m. p. 41·5—45·5°, from aqueous alcohol at 0° gave pentadec-14-enoic acid as plates, m. p. 49·1—49·3° (uncorr.) (Found : equiv., 241. Calc. for $C_{15}H_{28}O_2$: equiv., 240) (Chuit, Boelsing, Hausser, and Malet, *ibid.*, 1927, **10**, 113, give m. p. 49·8—50°). From the petroleum-insoluble portion sebacic acid (15 g., 34%) was obtained.

In another experiment the yield of pentadec-14-enoic acid was 30%.

Tetradecanedioic Acid.—A slow stream of ozonised oxygen (*ca.*, 3% O_3) was passed through a solution of pentadec-14-enoic acid (0·5 g.) in chloroform (10 c.c.) for 4 hr. The solvent was evaporated and the residue was heated with hydrogen peroxide (10% v/v; 20 c.c.), giving a solid (0·25 g., 47%), m. p. 118—122°. Crystallisation from benzene and finally from aqueous alcohol yielded the diacid, m. p. 125·5—126° (*idem, loc. cit.*, give m. p. 124·8—125·4°), undepressed on admixture with an authentic specimen (prepared by electrolysis of methyl hydrogen suberate and hydrolysis of the resulting diester).

Tetratriaconta-cis-9 : cis-25-*diene.*—Oleic acid (10 g.) in methanol (20 c.c.) was electrolysed in cell "A" (current 0·5 amp.; faradays passed, *ca.* 1·25 times theoretical). During the reaction much insoluble polymer was formed and a colourless oil separated. After the electrolysis, light petroleum (b. p. 60—80°) was added to the cell contents to dissolve the oil, and the warm mixture was then filtered, neutralised, and evaporated. The residue was extracted thoroughly (Soxhlet; 20 hr.) with light petroleum (b. p. 60—80°). Acidification of the insoluble residue yielded crude oleic acid (1·3 g.), m. p. 5—10°. Evaporation of the extract and distillation of

the residue (5·5 g.) gave : (i) Methyl oleate (2·0 g.), b. p. 70—95° (bath-temp.)/10^{-4} mm. (ii) An oil (2·0 g., 23%), b. p. 145—150° (bath-temp.)/10^{-4} mm., m. p. 18—19°. Two crystallisations at −20° from light petroleum (b. p. 40—60°) gave tetratriaconta-*cis*-9 : *cis*-25-diene as colourless needles, m. p. 21·5—22·0°, n_D^{33} 1·4589 (Found : C, 86·05; H, 14·15. Calc. for $C_{34}H_{68}$: C, 86·0; H, 14·0%) (Petersen, *Z. Elektrochem.*, 1912, **18**, 1711, gives m. p. 22·5°).

Tetratriaconta-trans-9 : trans-25-*diene*.—Elaidic acid (6·8 g.; m. p. 42—43°) in methanol (20 c.c.) was electrolysed in cell " A " (current 0·5 amp.; faradays passed *ca.* 1·25 times theoretical). During the reaction crystals separated; they had m. p. 51—53° (2·5 g., 44%). Crystallisation from alcohol–light petroleum (b. p. 60—80°) gave the *hydrocarbon* as rectangular plates, m. p. 55·5—56° (Found : C, 86·1; H, 13·7%). From the methanolic mother-liquors elaidic acid (0·4 g.) and methyl elaidate (1·5 g.), b. p. 90—110° (bath-temp.)/10^{-4} mm., n_D^{16} 1·4508—1·4521, were isolated. The latter, by hydrogenation and subsequent hydrolysis, was converted into stearic acid, m. p. and mixed m. p. 70°.

Erucic (*Docosa*-cis-13-*enoic*) *Acid*.—A mixture of oleic acid (20·7 g., 0·07 mole) and methyl hydrogen adipate (33 g.) in methanol (120 c.c.) was electrolysed in cell " B " (current 1·7 amp.; faradays passed, *ca.* 1·2 times theoretical). Towards the end of the reaction the current tended to drop but was restored at intervals to its former value by the addition of more half-ester (altogether 45·5 g., 0·28 mole, of the latter were used). After the electrolysis, the alkaline cell contents were acidified and then evaporated. The residue, in ether (500 c.c.), was washed with aqueous sodium hydroxide (2% w/v), then with water, and dried (Na_2SO_4). Evaporation of the solvent and distillation of the residual oil (38 g.) from a Kon flask gave : (i) Dimethyl sebacate (20·0 g.), b. p. 106—114°/6 × 10^{-4} mm., n_D^{32} 1·4241, which was contaminated with an unsaturated compound but gave sebacic acid (16 g., 57%), m. p. 131·5—133°, on hydrolysis. (ii) A fraction (11·6 g.), b. p. 180—191°/6 × 10^{-4} mm., n_D^{20} 1·4552, consisting largely of methyl erucate. Hydrolysis furnished a solid mixture of sebacic and erucic acids. Extraction with light petroleum (b. p. 60—80°; 40 c.c.), and evaporation of the extract, yielded erucic acid (8·0 g., 34%) as needles, m. p. 29—30°.

Further purification of the erucic acid was effected in the following manner. The acid was converted into its *lithium* salt which after extraction with ether (Soxhlet; 10 hr.) and four crystallisations from 60% aqueous alcohol had m. p. 222—226° (uncorr., sealed capillary), unaltered by further recrystallisation (Found : Li, 2·4. $C_{22}H_{41}O_2Li$ requires Li, 2·0%). The salt was shaken with dilute hydrochloric acid and ether; the ethereal layer was washed with water, dried, and evaporated, giving the free acid (3·8 g.), m. p. 31·7—32·2° (Found : equiv., 338·5. Calc. for $C_{22}H_{42}O_2$: equiv., 338·5), raised to 32·5—33° by crystallisation from alcohol at 0° (Found : C, 77·75; H, 12·45. Calc. : C, 78·0; H, 12·5%) (Skellon and Taylor, *J.*, 1952, 1813, give m. p. 33·0°). The *p*-bromophenacyl ester crystallised from alcohol in needles, m. p. 62° (Ames and Bowman, *J.*, 1950, 177, give m. p. 62°).

The residue from the preceding distillation was distilled from a short-path still and yielded tetratriaconta-*cis*-9 : *cis*-25-diene (2·7 g., 16%), b. p. 145—155° (bath-temp.)/10^{-4} mm., m. p. 18—19°, n_D^{22} 1·4640.

Brassidic (*Docos*-trans-13-*enoic*) *Acid*.—A mixture of elaidic acid (15 g., 0·053 mole; m. p. 44·0—44·3°) and methyl hydrogen adipate (25 g.) in methanol (90 c.c.) was electrolysed in cell " B " (current 1·7 amp.; faradays passed, *ca.* 1·2 times theoretical). At intervals towards the end of the reaction more half-ester was added (total used 34 g., 0·21 mole). The tetratriaconta-*trans*-9 : *trans*-25-diene (1·3 g.), m. p. 54—55°, which separated during the electrolysis was collected. (A further 0·3 g. was obtained by crystallisation of the high-boiling residues from the distillation of the other products; total yield 13%.) The cell contents were acidified and evaporated and the residue was separated into acidic and neutral fractions in the usual way. From the former elaidic acid (3·0 g.), m. p. 41—42°, was recovered. Distillation of the neutral fraction gave : (i) Liquid (14 g.), b. p. 115—125°/0·8 mm., n_D^{19} 1·4394, which on hydrolysis yielded sebacic acid (13 g., 60%). (ii) Methyl brassidate (7·1 g.), b. p. 175—185°/0·5 mm., m. p. 27—29° (Keffler and Maiden, *J. Phys. Chem.*, 1936, **40**, 905, give m. p. 30·1°), n_D^{35} 1·4495, which was hydrolysed, the resulting acid being extracted with light petroleum (b. p. 60—80°; 150 c.c.). Evaporation of the extract yielded a solid (6·1 g., 34%), m. p. 57—58° (Found : equiv., 344). Crystallisation (charcoal) from alcohol gave brassidic acid (4·1 g.) as rhombs, m. p. 59·8—60·0° (Found : C, 78·1; H, 12·6; equiv., 338. Calc. for $C_{22}H_{42}O_2$: C, 78·0; H, 12·5%; equiv., 338·5) (Sudborough and Gittins, *J.*, 1909, **95**, 320, give m. p. 59·5—60°). The *p*-bromophenacyl ester crystallised from alcohol in plates, m. p. 73° (Ames and Bowman, *loc. cit.*, give m. p. 74°).

Tetratriaconta-threo-9 : 10-threo-25 : 26-*tetrol*.—(*a*) A warm (45—55°) solution of *threo*-

9 : 10-dihydroxystearic acid (31·6 g.) in methanol (140 c.c.) was electrolysed in cell " C " (a current of 1·2 amps. was used initially but this fell to 0·5 amp. when the product began to separate; total faradays passed, *ca.* 4·5 times theoretical). The cell contents were cooled to 20° and the product (13·7 g., 50%), m. p. 120·5—123°, was collected. Crystallisation from alcohol gave the microcrystalline tetrol (9·7 g.), m. p. 124—124·5° (Found : C, 75·45; H, 13·0. Calc. for $C_{34}H_{70}O_4$: C, 75·4; H, 13·0%) (D.R.-P. 624,331 gives m. p. 121°).

Neutralisation and evaporation of the methanolic mother-liquors gave a semi-solid (11·0 g.) from which no pure product could be isolated.

(*b*) A mixture of tetratriaconta-*cis*-9 : *cis*-25-diene (0·5 g.), aqueous hydrogen peroxide (25—30%; *ca.* 15% excess) and formic acid (98—100%; 6 c.c.) was stirred vigorously at 40° for 4 days (cf. Swern, Billen, and Scanlan, *J. Amer. Chem. Soc.*, 1946, **68**, 1504). Water (35 c.c.) was added and the solid precipitate was collected, washed with water, and hydrolysed by hot aqueous-methanolic 2N-sodium hydroxide for 2 hr. The resulting mixture was concentrated and acidified with 2N-sulphuric acid. The solid (0·37 g., 70%) was collected and had m. p. 119—121°. Crystallisation from alcohol gave the tetrol, m. p. 123—124° (57%), undepressed on admixture with a specimen from (*a*).

Tetratriaconta-erythro-9 : 10-erythro-25 : 26-*tetrol*.—(*a*) *erythro*-9 : 10-Dihydroxystearic acid (20 g.) in methanol (360 c.c.) was electrolysed in cell " C " (current 1·4 amp.; faradays passed, *ca.* 11 times theoretical). The product (3·3 g., 20%), which separated during the reaction, was collected and had m. p. 162—163°. Crystallisation from alcohol gave the microcrystalline *tetrol*, m. p. 163·5—164° (Found : C, 75·7; H, 13·1. $C_{34}H_{70}O_4$ requires C, 75·4; H, 13·0%). Evaporation of the methanolic mother-liquors gave a solid (13·5 g.) from which no pure product could be isolated.

(*b*) A solution of performic acid [prepared from 98—100% formic acid (7·0 c.c.) and 25—30% hydrogen peroxide (0·24 c.c.)] was added to tetratriaconta-*trans*-9 : *trans*-25-diene (0·35 g.) in chloroform (20 c.c.). The mixture was warmed to 40°, acetone (1 c.c.) was added, and the resulting homogeneous solution was stirred at 40° for 20 hr. (a further 0·2 c.c. of hydrogen peroxide was added after 12 hr.). Evaporation of the solvents, hydrolysis of the residue and isolation of the product in the usual way gave a solid (0·3 g., 75%), m. p. 157·5—160·5°. Two crystallisations from alcohol–ethyl acetate gave the tetrol, m. p. 164°, undepressed on admixture with a specimen from (*a*).

Attempts to hydroxylate the diene in heterogeneous media by the method described above for the *cis-cis*-isomer were unsuccessful, the starting material being recovered unchanged even after 4 days.

Oxidation of the Tetrols.—(*a*) Freshly prepared lead tetra-acetate (24·1 g., 0·054 mole) was added during 1·5 hr. in small portions to a well-stirred solution of the tetrol, m. p. 124° (15 g., 0·028 mole) in benzene (450 c.c.) and acetic acid (" AnalaR; " 38 c.c.) which was kept at 65° in an atmosphere of nitrogen. The mixture was stirred at 65° for a further 3 hr. and then cooled. The tetra-acetate-free solution was decanted from the lead acetate, and the latter was washed with warm benzene (40 c.c.). The benzene solutions were combined, washed with water until free from acetic acid, dried (Na_2SO_4), and evaporated under reduced pressure (Dufton column). A portion (4 g.) of the residue (15 g.) was distilled, giving nonanal (1·1 g., 51%), b. p. 60—64°/7 mm., n_D^{20} 1·4235. The 2 : 4-dinitrophenylhydrazone (formed in 84% yield) had m. p. 105·5°, undepressed on admixture with an authentic specimen (Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730, gives m. p. 105—106°).

Potassium permanganate (11·0 g.) was added in small portions during 3·5 hr. to a well-stirred and cooled (15°) suspension of the remainder of the crude product in water (90 c.c.) and sulphuric acid (9·4 c.c.) (cf. Ruhoff, *Org. Synth.*, 1936, **16**, 39). The resulting mixture was treated with sulphur dioxide until all the manganese dioxide had reacted. The organic layer was separated and extracted with light petroleum (b. p. 60—80°; 60 c.c.). Crystallisation of the residue (2·4 g., 43%), m. p. 117—120°, from benzene gave thapsic acid, m. p. 123—123·5°, undepressed on admixture with an authentic specimen. Distillation of the petroleum extract yielded nonanoic acid (2·3 g., 35%), b. p. 140—142°/16 mm., m. p. 8—10°, n_D^{24} 1·4319. The *p*-toluidide crystallised from alcohol in needles, m. p. 83·5—84° (Robertson, *J.*, 1919, **115**, 1221, gives m. p. 84°).

(*b*) Similar oxidation of the tetrol, m. p. 164°, (2·0 g.) gave nonanal (48%) (2 : 4-dinitrophenylhydrazone) and thapsic acid (34%).

threo-13 : 14-*Dihydroxybehenic* (*Dihydroxydocosanoic*) *Acid*.—A solution of *threo*-9 : 10-dihydroxystearic acid (60 g., 0·19 mole) and methyl hydrogen adipate (122 g., 0·76 mole) in methanol (710 c.c.) was electrolysed in cell " C " (current 4·3 amp.). After 6 hr. a solid separated

from the electrolyte; the current fell markedly but was restored to its former value by the addition of more half-ester (30 g., 0·2 mole) (faradays passed, *ca.* 1·5 times theoretical). After the electrolysis, the solid was collected, giving tetratriaconta-*threo*-9 : 10-*threo*-25 : 26-tetrol (7 g., 14%). The filtrate was neutralised with dilute hydrochloric acid and then evaporated. The residue was extracted with ether. On acidification of the insoluble residue *threo*-9 : 10-dihydroxystearic acid (6·0 g.) was recovered. The ethereal extract was washed with aqueous sodium hydroxide (2% w/v), dried, and evaporated. Distillation gave dimethyl sebacate (59 g., 54%), b. p. 110—120°/0·07 mm., n_D^{20} 1·4377. The high-boiling residue was hydrolysed with methanolic sodium hydroxide (10% w/v), and the acidic product was isolated, washed twice with boiling water, dried, and extracted with warm benzene (125 c.c.). The sodium salt of the residual acid (21 g., 30%), m. p. 99—100°, was extracted with benzene (Soxhlet; 12 hr.). Regeneration of the free acid and crystallisation from methanol gave *threo*-13 : 14-dihydroxybehenic acid (17 g., 24%) as plates, m. p. 100·5—101° (Found: C, 71·05; H, 12·0%; equiv., 374. Calc. for $C_{22}H_{44}O_4$: C, 70·9; H, 11·9%; equiv., 373) (Dorée and Pepper, *J.*, 1942, 477, give m. p. 101°).

erythro-13 : 14-*Dihydroxybehenic Acid*.—A solution of *erythro*-9 : 10-dihydroxystearic acid (34·5 g., 0·11 mole) and methyl hydrogen adipate (64 g., 0·40 mole) in methanol (500 c.c.) was electrolysed in cell " C." At intervals more half-ester (total used 85 g.; 0·52 mole) was added (current, 3—4 amp.; faradays passed, *ca.* 1·5 times theoretical). After the electrolysis tetratriaconta-*erythro*-9 : 10-*erythro*-25 : 26-tetrol (4·5 g., 15%), which had separated during the reaction from the warm (40°) electrolyte, was collected. When kept at 20° the filtrate deposited a solid which was collected and crystallised from methanol, giving methyl *erythro*-13 : 14-dihydroxybehenate (12·0 g., 29%), m. p. 107—107·5° (Found: C, 71·45; H, 12·15. Calc. for $C_{23}H_{46}O_4$: C, 71·45; H, 12·0%). Hydrolysis with ethanolic sodium hydroxide (10% w/v) gave the dihydroxy-acid (10·2 g.) as hexagonal plates, m. p. 128·5—129·5°, raised to 130° by crystallisation from methanol (Found: C, 71·15; H, 12·1%; equiv., 374. Calc. for $C_{22}H_{44}O_4$: C, 70·9; H, 11·9%; equiv., 373) (Albitski, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 788, gives m.p. 130—131°).

From the methanolic mother-liquors, after removal of the crystalline dihydroxy-ester, *erythro*-9 : 10-dihydroxystearic acid (4·7 g.), dimethyl sebacate (60 g., 54%), and *erythro*-13 : 14-dihydroxybehenic acid (2·4 g., total yield 33%) were obtained by procedures similar to those outlined in the preceding experiment.

Oxidation of the 13 : 14-*Dihydroxybehenic Acids* (cf. Huber, *loc. cit.*).—(*a*) Oxidation of the *threo*-compound (1·0 g.) with periodic acid and steam-distillation of the product gave nonanal. The 2 : 4-dinitrophenylhydrazone (formed in 23% overall yield) crystallised from alcohol in needles, m. p. 103—104°, undepressed on admixture with an authentic specimen.

Permanganate oxidation of the residue from the steam-distillation yielded a solid (0·32 g., 49%), m. p. 104—107°, which was crystallised several times from benzene and gave brassylic (tridecanedioic) acid, m. p. 112·5—113·5° (Found: equiv., 124. Calc. for $C_{13}H_{24}O_4$: equiv., 122) (Chuit, *Helv. Chim. Acta*, 1926, **9**, 264, gives m. p. 113—113·2°).

(*b*) Similar degradation of the *erythro*-compound (2·0 g.) gave nonanal 2 : 4-dinitrophenylhydrazone (0·86 g., 37%) and brassylic acid (0·46 g., 35%) (Found: equiv., 124).

Brassidic Acid (cf. Ames and Bowman, *J.*, 1951, 1804).—Concentrated sulphuric acid (20 c.c.) was added in small portions to a cooled mixture of *threo*-13 : 14-dihydroxybehenic acid (2·5 g.) in a solution of hydrogen bromide in acetic acid (20% w/v; *d* 1·3; 21 c.c.). The mixture was kept for 21 hr. and then heated at 100° for 8 hr. Half way through the latter period more hydrogen bromide–acetic acid (2 c.c.) was added. The mixture was poured into water, and the product was isolated with light petroleum (b. p. 60—80°), giving a pale yellow acid (3·2 g.), which was esterified by heating it with alcohol, sulphuric acid, and benzene, the water formed being removed by azeotropic distillation. The resulting crude ester, in light petroleum (b. p. 40—60°; 100 c.c.) was poured on to a column of alumina (7 × 1″) and eluted with the same solvent (400 c.c.). Evaporation of the eluate gave a solid (1·83 g., 52%), m. p. 35·5—37°, which was crystallised twice from alcohol at 0°, yielding *ethyl* erythro-13 : 14-*dibromobehenate*, m. p. 37—37·5° (Found: C, 55·1; H, 8·85. $C_{24}H_{46}O_2Br_2$ requires C, 54·85; H, 8·8%).

A well-stirred mixture of the dibromo-ester (1·2 g.), alcohol (12 c.c.), and activated zinc dust (2·3 g.) was boiled under reflux for 1½ hr. in an atmosphere of nitrogen. The mixture was filtered and the solid was washed well with light petroleum (b. p. 60—80°). The filtrate was diluted with water and the product was isolated with light petroleum (b. p. 60—80°). Distillation yielded ethyl brassidate (0·54 g., 70%), b. p. 145—150°/5 × 10^{-5} mm., m. p. 23·7—24°,

n_D^{24} 1·4612, which after two crystallisations from acetone at −15° was obtained as rhombs, m. p. 24·5° (Found: C, 78·1; H, 12·8. Calc. for $C_{24}H_{46}O_2$: C, 78·6; H, 12·65%) (Keffler and Maiden, *loc. cit.*, give m. p. 25·0°). Hydrolysis with ethanolic sodium hydroxide, and isolation of the acidic fraction, gave a solid (82%), m. p. 57·5—58·5°. Crystallisation from alcohol yielded brassidic acid as plates, m. p. 59·5—60° (Found: C, 77·85; H, 12·6%; equiv., 341. Calc. for $C_{22}H_{42}O_2$: C, 78·0; H, 12·5%; equiv., 339). The *p*-bromophenacyl ester had m. p. 73°.

Erucic Acid.—erythro-13 : 14-Dihydroxybehenic acid (6·0 g.) was converted into *threo*-13 : 14-dibromobehenic acid (5·7 g.) which was esterified, giving the *ethyl ester* (4·3 g., 51%), b. p. 125—130°/10^{-4} mm., n_D^{20} 1·4826 (Found: C, 54·85; H, 8·95. $C_{24}H_{46}O_2Br_2$ requires C, 54·75; H, 8·8%).

Debromination of the ester (3·8 g.) in alcohol with zinc gave ethyl erucate (2·4 g., 91%), b. p. 110—115°/10^{-4} mm., n_D^{21} 1·4550 (Found: C, 79·05; H, 12·8. Calc. for $C_{24}H_{46}O_2$: C, 78·6; H, 12·65%). Hydrolysis and isolation of the acidic product gave erucic acid (1·73 g., 93%), as needles m. p. 32—32·5°, raised to 33° by crystallisation from methanol at 0° (Found: C, 77·8; H, 12·55. Calc. for $C_{22}H_{42}O_2$: C, 78·0; H, 12·5%).

The m. p.s of both specimens of synthetic erucic acid reported above were undepressed on admixture with an authentic sample of the natural acid, for which the authors are indebted to Dr. J. H. Skellon.

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488. *Hydrophilic Derivatives of 4-Aminodiphenyl.*

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In order to obtain derivatives of 4-aminodiphenyl containing water-solubilising groups, 2-*p*-diphenylylaminoethanol and 3-*p*-diphenylylaminopropane-1 : 2-diol have been prepared; the former alcohol could be obtained in 70% overall yield from 4-aminodiphenyl by hydroxyethylation of *N*-*p*-diphenylyltoluene-*p*-sulphonamide. *N*-*p*-Diphenylylethylamine has been obtained by two methods from 4-acetamidodiphenyl. The basic strengths and oil–water partition coefficients at pH 7·2 of these bases, as well as of the related 4-(*NN*-bis-2-hydroxyethylamino)diphenyl and 4-dimethylaminodiphenyl, have been determined, and the results are discussed.

For investigation of the effect on antituberculous activity when water-solubility is increased and the lipoid–water partition coefficient decreased, some derivatives of 4-aminodiphenyl containing water-solubilising groups such as hydroxy- or dihydroxy-alkyl were required.

2-*p*-Diphenylylaminoethanol was prepared (Baxter and Cymerman-Craig, *J.*, 1953, 1940) in 36% yield by reaction of 2-bromoethanol with *N*-4-benzylideneaminodiphenyl, followed by acid hydrolysis. Reaction of 4-aminodiphenyl with 2-bromoethanol in 2-ethoxyethanol gave only (64%) 4-(*NN*-bis-2-hydroxyethylamino)diphenyl, previously obtained by Ross (*J.*, 1949, 184). The same reaction, carried out in acetone solution, gave a 39% yield of this compound, as well as 4% of the desired monoalcohol. If 2-chloroethanol was used, only 6% of bishydroxyethyl compound was formed in 2-ethoxyethanol solution; no reaction occurred in acetone.

Treatment of the sodium salt of *N*-*p*-diphenylyltoluene-*p*-sulphonamide with 2-bromoethanol gave 84% of a 1 : 1 molecular compound, m. p. 131° of the starting sulphonamide and the desired *N*-*p*-diphenylyl-*N*-2′-hydroxyethyltoluene-*p*-sulphonamide. Attempts to resolve this complex by treatment with sodium hydroxide failed. However, prolonged hydrolysis with 24% hydrochloric acid readily gave 84% of 2-*p*-diphenylylaminoethanol (overall yield 70·5%), and 63% of unchanged sulphonamide. Molecular-weight determin-

ations of the complex gave 350 (Rast) and 341 (cryoscopic in benzene) respectively, almost exactly the mean of the molecular weights of the two components (345), indicating complete dissociation in solution, from which however it crystallises unchanged.

Two substances of similar structure but without the hydrophilic group were also prepared. Alkylation of 4-acetamidodiphenyl with ethyl iodide gave 24% of *N*-*p*-diphenylylethylamine, also obtained in 87% yield by lithium aluminium hydride reduction of the amide.

Several analogues of glycerol, including 3-aminopropane-1 : 2-diol, have been found by Bloch, Matter, and Suter (*Amer. Rev. Tuberc.*, 1947, **55**, 540) to increase the oxygen uptake of the tubercle bacillus, and Baker, Querry, and Kadish (*J. Org. Chem.*, 1950, **15**, 402) have prepared 4-amino-4′-(2 : 3-dihydroxypropylamino)diphenyl sulphone. Reaction of 4-aminodiphenyl with glycidol (Rider and Hill, *J. Amer. Chem. Soc.*, 1930, **52**, 1525) readily afforded the water-soluble 3-*p*-diphenylylaminopropane-1 : 2-diol in 88·5% yield. The presence of a catalytic amount of pyridine reduced the yield to 70%.

The basic strengths of the amines were determined in 50% aqueous-alcoholic solution by potentiometric titration (Carswell, Cymerman, and Lyons, *J.*, 1952, 430). Calculations were carried out by means of equation (1) which takes into account the effect of hydrogen ion; in the low concentrations used, this correction becomes appreciable at pH values below 4. The results are shown in Table 1.

$$pK_a = pH - \log \frac{[B] + [H^+]}{[BH^+] - [H^+]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is seen that increase in basic strength resulting on substitution of the amino-group in 4-aminodiphenyl by two methyl groups or one ethyl group is paralleled by that occurring in the corresponding anilines (Hall and Spinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3472). The lowering of pK_a due to the introduction of a 2-hydroxyethyl group, known to possess $+I$ character (Dewar, "The Electronic Theory of Organic Chemistry," Oxford, 1949), is clearly shown in the diphenyl series, and also by ethylamine, aminoethanol, and bishydroxyethylamine. Whereas introduction of a hydroxyl group directly on the nitrogen atom of a base depresses the pK_a by 3·25 units (ammonia 9·25; hydroxylamine 6·0), the same group on the β-carbon atom of an *N*-ethyl group depresses pK_a by only 0·77 unit, and in the γ-position, as in 3-*p*-diphenylylaminopropane-1 : 2-diol, further by only 0·41 unit.

TABLE 1. *Ionisation of substituted 4-aminodiphenyls in 50% alcohol at 20° ± 1°.*

Compound	pK_a	Compound	pK_a
$C_6H_4Ph{\cdot}NH_2$	4·05 [1]	NH_2Ph	4·58 [2]
$C_6H_4Ph{\cdot}NMe_2$	4·47	$NPhMe_2$	5·06 [2]
$C_6H_4Ph{\cdot}NHEt$	4·52	$NHPhEt$	5·11 [2]
$C_6H_4Ph{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	3·75	NH_2Et	10·62 [2]
$C_6H_4Ph{\cdot}N(CH_2{\cdot}CH_2{\cdot}OH)_2$	3·20	$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	9·09 [2]
$C_6H_4Ph{\cdot}NH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$	3·34	$NH(CH_2{\cdot}CH_2{\cdot}OH)_2$	8·88 [2]

[1] Carswell, Cymerman, and Lyons, *J.*, 1952, 430. [2] Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3472. Measurement in water at 25°.

TABLE 2. *Oil–water partition coefficients of substituted 4-aminodiphenyls between liquid paraffin and phosphate buffer* (pH 7·2) *at 20° ± 2°.*

Compound	k'	$\lambda_{max.}$ (mμ)	log ε	Compound	k'	$\lambda_{max.}$ (mμ)	log ε
$C_6H_4Ph{\cdot}NHEt$	1550	282	4·33	$C_6H_4Ph{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	2·65	282·5	4·29
$C_6H_4Ph{\cdot}NH_2$	92	270	4·21	$C_6H_4Ph{\cdot}N(CH_2{\cdot}CH_2{\cdot}OH)_2$	0·26	300	4·32
				$C_6H_4Ph{\cdot}NH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$	0·085	283·5	4·28

The partition coefficients between liquid paraffin (B.P., 1932) and water at pH 7·2 (the physiological pH) were determined by the spectrophotometric method of Cymerman-Craig and Diamantis (*J.*, 1953, 1619), and the value of the apparent partition coefficient (k') is given in Table 2, together with the wave-length of the absorption maximum and the intensity of absorption. Table 2 shows the stepwise increase in hydrophilic properties caused by the introduction of one or two 2-hydroxyethyl groups or the 2 : 3-dihydroxypropyl group, as well as the corresponding increase in lipophilic nature resulting on

substitution of the amino-group in 4-aminodiphenyl by two methyl groups or one ethyl group. Since the pK_a of the bases in Table 2 does not exceed 4·5, it follows that, as shown by equation (2) (Cymerman-Craig and Diamantis, *loc. cit.*), the apparent partition coefficient (k') measured in this determination is equal to the true partition coefficient (k) for these compounds.

$$k/k' = 1 + \text{antilog}\ (pK_a - pH) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The activities *in vitro* of the bases in Table 2, kindly determined by Professor S. D. Rubbo, were uniformly low, complete inhibition of bacterial growth of *Mycobact. tuberculosis* (H37Rv), in the presence of 10% of serum, requiring dilutions of M/2000 to M/4000; an account of the bacteriological aspects will be given elsewhere. Variation in partition coefficient thus appears to have no effect on activity in this series.

Experimental

2-p-*Diphenylylaminoethanol* [with W. S. Gilbert].—(*a*) A mixture of 4-aminodiphenyl (17 g., 0·1 mol.), 2-bromoethanol (18·7 g., 0·15 mol.), and powdered calcium carbonate (5 g.) was refluxed with 2-ethoxyethanol (150 c.c.) and water (10 c.c.) for 31·5 hr. The solution was cooled, made alkaline to brilliant-yellow with sodium hydroxide (2N), and filtered. The filtrate was evaporated to low bulk *in vacuo* and the crystalline precipitate triturated with water (100 c.c.) and filtered off. Crystallisation from 95% alcohol afforded nacreous plates, m. p. 154°, of 4-(*NN*-bis-2-hydroxyethylamino)diphenyl (12·4 g., 64% calc. on 2-bromoethanol) (Found: C, 74·2, 74·45; H, 7·85, 7·3; N, 5·35; O, 12·5. Calc. for $C_{16}H_{19}O_2N$: C, 74·65; H, 7·45; N, 5·45; O, 12·45%), insoluble in boiling ether. Ross (*J.*, 1949, 184) gives m. p. 149—151°. From ethyl acetate the *hydrochloride* crystallised in needles, m. p. 191·5—192° (Found: C, 65·6; H, 6·95; N, 4·65. $C_{16}H_{19}O_2N,HCl$ requires C, 65·4; H, 6·85; N, 4·75%), and the *picrate* as needles, m. p. 153° (Found: C, 54·35, 54·4; H, 4·55, 4·6; N, 11·4, 11·6. $C_{16}H_{19}O_2N,C_6H_3O_7N_3$ requires C, 54·35; H, 4·55; N, 11·5%).

(*b*) A similar preparation from 4-aminodiphenyl (17 g.), 2-bromoethanol (18·7 g.), and anhydrous potassium carbonate (6·9 g.), refluxed in dry acetone (100 c.c.) for 28·5 hr., gave 7·9 g. (39%), m. p. 154°, identical with the material obtained as in (*a*). The mother-liquors were treated with excess of sodium hydroxide solution and extracted with ether. The dried ethereal extracts gave (apart from unchanged 4-aminodiphenyl) 0·8 g. (4%) of 2-*p*-diphenylylaminoethanol, crystallising from light petroleum (b. p. 60—90°) as needles, m. p. 111·5—113° (Found: C, 78·35; H, 6·95; N, 7·0. Calc. for $C_{14}H_{15}ON$: C, 78·85; H, 7·1; N, 6·6%). Baxter and Cymerman-Craig (*J.*, 1953, 1940) give m. p. 112°.

Reaction of N-(4-*Diphenylyl*)*toluene*-p-*sulphonamide with* 2-*Bromoethanol.*—To a solution of sodium ethoxide [from sodium (1·8 g.) in absolute alcohol (300 c.c.)] was added *N*-*p*-diphenylyltoluene-*p*-sulphonamide (25·85 g.), the sodium salt crystallising. After addition of 2-bromoethanol (10 g.) in absolute alcohol (100 c.c.) the mixture was refluxed for 5 hr. The clear solution was evaporated and gave, after removal of sodium bromide, 23·2 g. (84%) of a product, m. p. 129—130°, crystallising from *iso*propanol as needles, m. p. 130·5—131°, of a molecular *compound* (1 : 1) of *N*-(4-diphenylyl)toluene-*p*-sulphonamide and *N*-(2-hydroxyethyl)-*N*-(4-diphenylyl)toluene-*p*-sulphonamide [Found: C, 69·55, 69·65; H, 5·75, 5·55; N, 4·85; S, 9·4, 9·3, 9·45; O, 11·5%; *M*, (Rast) 350, (cryoscopic, C_6H_6) 341. $C_{19}H_{17}O_2NS,C_{21}H_{21}O_3NS$ requires C, 69·55; H, 5·55; N, 4·1; S, 9·3; O, 11·6%; *M*, 690. Calc. for $C_{21}H_{21}O_3NS$: C, 68·65; H, 5·75; N, 3·8; S, 8·7; O, 13·05%; *M*, 367. Calc. for $C_{19}H_{17}O_2NS$: C, 70·55; H, 5·3; N, 4·35; S, 9·9; O, 9·9%; *M*, 323].

2-p-*Diphenylylaminoethanol.*—The molecular compound (m. p. 130·5—131°; 13·1 g.) was refluxed for 18 hr. with hydrochloric acid (180 c.c.; 24% w/v) and filtered hot. The residue (R) was extracted with boiling water (200 c.c.) and the combined filtrates were cooled, basified, and extracted with ether. Evaporation of the dried (Na_2SO_4) ethereal extracts gave 3·35 g. (83%) of 2-*p*-diphenylylaminoethanol, m. p. 111·5—112°. The residue (R) (3·85 g., 63%) was *N*-(4-diphenylyl)toluene-*p*-sulphonamide, m. p. 153—154°, undepressed on admixture with an authentic sample (m. p. 158°).

N-p-*Diphenylylethylamine.*—(*a*) A mixture of 4-acetamidodiphenyl (6·33 g.), dry xylene (50 c.c.) and sodium (0·7 g.) was refluxed for 2·5 hr., cooled, and, after the addition of ethyl iodide (3·5 c.c., 50% excess), refluxed for a further 0·5 hr. After removal of the xylene by distillation, the residue was poured into water and extracted with ether. The residue left on evaporation of the washed and dried (Na_2SO_4) ethereal extracts was refluxed with alcoholic

potassium hydroxide (50 c.c.; 1% w/v) for 7 hr. The mixture was poured into water and extracted with ether. Dry hydrogen chloride was passed into the dried ethereal solution, giving 1·65 g. (24%) of N-p-*diphenylylethylammonium chloride*, crystallising from 95% alcohol as prisms, m. p. 208—209° (Found: C, 71·9; H, 6·85; N, 6·4. $C_{14}H_{16}NCl$ requires C, 71·95; H, 6·9; N, 6·0%). Treatment of this with aqueous alkali gave N-p-*diphenylylethylamine*, crystallising from light petroleum (b. p. 40—70°) as plates, m. p. 67—69° (Found: N, 7·25. $C_{14}H_{15}N$ requires N, 7·1%).

(*b*) A solution of 4-acetamidodiphenyl (2·5 g.) in dry ether (500 c.c.) was refluxed with lithium aluminium hydride (0·3 g.) for 13·5 hr. The complex was decomposed by successive addition of water, sodium hydroxide solution, and ammonium chloride, and the mixture extracted with ether. The residue left on evaporation of the dried (Na_2SO_4) extracts was refluxed with light petroleum (b. p. 40—70°; 50 c.c.) and filtered, leaving unchanged 4-acetamidodiphenyl (1·15 g., 46%), m. p. 167·5—168°, undepressed on admixture with an authentic sample (m. p. 169·5—170°). The filtrate gave *N-p*-diphenylylethylamine (1·1 g., 87% calc. on acetamidodiphenyl which reacted), m. p. 66—68°, undepressed on admixture with the material obtained by method *a*.

N-4-*Diphenylyl*-NN-*dimethylammonium chloride* had m. p. 129° (decomp.) (Found: N, 5·9. $C_{14}H_{15}N,HCl$ requires N, 6·0%).

3-p-*Diphenylylaminopropane*-1 : 2-*diol*.—4-Aminodiphenyl (6·76 g., 0·04 mol.) and glycidol (2·96 g., 0·04 mol.) were heated at 100° for 4 hr. Trituration with ether or light petroleum (b. p. 40—70°) gave a white solid (8·6 g., 88·5%), m. p. 103—108°, almost insoluble in boiling ether but soluble in hot benzene and hot water. Crystallisation from aqueous alcohol gave plates, m. p. 128°, of 3-p-*diphenylylaminopropane*-1 : 2-*diol* (Found: N, 5·95. $C_{15}H_{17}O_2N$ requires N, 5·75%). The *hydrochloride* crystallised from ethanol in plates, m. p. 186° (Found: N, 5·3%; equiv., 273. $C_{15}H_{17}O_2N,HCl$ requires N, 5·0%; equiv., 280).

We express our gratitude to Professor S. D. Rubbo and Miss B. Pierson for the bacteriological examination of these substances. This work was carried out under the auspices of the National Health and Medical Research Council, whom we thank for financial assistance. We also acknowledge the award to one of us (J. N. B.) of a Monsanto (Aust.) Pty. Ltd., Scholarship, and thank Mrs. E. Bielski for microanalyses.

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489. *Reactions in Fused Aluminium Chloride–Sodium Chloride.*

By D. B. BRUCE, A. J. S. SORRIE, and R. H. THOMSON.

It is shown that intramolecular cyclisations, Fries rearrangements, and condensation of quinol with various mono- and di-basic acids can be effected in two minutes by fusion in an aluminium chloride–sodium chloride melt at 180—200°. Condensation of quinol with γ-butyro- and valero-lactones gave indanones and not the expected tetralones.

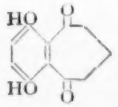
A MOLTEN mixture of aluminium chloride and sodium chloride has been used in the synthesis of naphthazarins and hydroxyanthraquinones by condensation of maleic and phthalic anhydrides with various phenols (Zahn and Ochwat, *Annalen*, 1928, **462**, 72; Kuroda and Wada, *Proc. Imp. Acad. Tokyo*, 1936, **12**, 239; Raudnitz, *Ber.*, 1929, **62**, 509; Waldmann and Mathiowetz, *J. pr. Chem.*, 1930, **126**, 250), and for the preparation of numerous more complex polycyclic quinones and ketones by cyclisation reactions involving dehydration and dehydrogenation (Scholl reactions). We now find that intramolecular cyclisations of aryl-substituted aliphatic acids, and Fries rearrangements, can be readily effected by this reagent by 2 minutes' heating at 180—200°. The method is convenient for small-scale (<10 g.) preparations but is limited by the fact that alkyl groups are known to migrate under such conditions (Auwers, *Annalen*, 1928, **460**, 254; Baddeley, *J.*, 1943, 273; 1944, 232; 1952, 2415). The yields recorded in the Table are similar to those obtained by more conventional procedures, any decrease being offset by the ease of operation in most cases.

Section (*c*) shows a number of ketones which were obtained by condensation of quinol with various carboxylic acids and lactones, and section (*d*) illustrates the cyclisation of aryl vinyl ketones under the same conditions. The condensation of quinols with dibasic acids

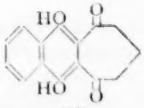
Reactants	Products	Yield, %
(*a*) *Cyclisation of aryl-substituted aliphatic acids* [1]		
β-Phenylpropionic acid	Indan-1-one	85
β-*m*-Hydroxyphenylpropionic acid	5-Hydroxyindan-1-one	60
	7-Hydroxyindan-1-one	15
β-*o*-Nitrophenylpropionic acid	4-Nitroindan-1-one	10
γ-Phenylbutyric acid	α-Tetralone	73
δ-Phenylvaleric acid	Benzosuberone	22
αβ-Diphenylsuccinic acid	1-Keto-2-phenylindan-3-carboxylic acid	50
(*b*) *Fries rearrangements* [2]		
Phenyl acetate	*o*-Hydroxyacetophenone	37
	p-Hydroxyacetophenone	35
Phenyl benzoate	*o*-Hydroxybenzophenone	17
	p-Hydroxybenzophenone	55
Quinol diacetate	2 : 5-Dihydroxyacetophenone	60
Quinol dibenzoate	2 : 5-Dihydroxybenzophenone	30
Quinol dicrotonate	4 : 7-Dihydroxy-3-methylindan-1-one	55
Phloroglucinol triacetate	Triacetylphloroglucinol	50
(*c*) *Phenol–acid condensations* (HQ = quinol)		
Phenol + benzoic acid	*o*-Hydroxybenzophenone	17
	p-Hydroxybenzophenone	55
HQ + benzoic acid	2 : 5-Dihydroxybenzophenone	33
HQ + *p*-bromobenzoic acid	4-Bromo-2′ : 5′-dihydroxybenzophenone	32
HQ + crotonic acid	4 : 7-Dihydroxy-3-methylindan-1-one	30
HQ + γ-butyrolactone	4 : 7-Dihydroxy-3-methylindan-1-one	45
HQ + γ-valerolactone	3-Ethyl-4 : 7-dihydroxyindan-1-one	12
HQ + maleic acid	Naphthazarin	30
HQ + succinic acid	1 : 2 : 3 : 4-Tetrahydro-5 : 8-dihydroxy-1 : 4-diketonaphthalene	25
HQ + glutaric acid	1′ : 4′-Dihydroxy-1 : 2-benzo*cyclo*heptene-3 : 7-dione	33
1 : 4-Dihydroxynaphthalene + glutaric acid	1′ : 4′-Dihydroxynaphtho(2′ : 3′-1 : 2)*cyclo*heptene-3 : 7-dione	7
HQ + adipic acid	δ-(2 : 5-Dihydroxybenzoyl)valeric acid	9
(*d*) *Cyclisation of aryl vinyl ketones* [3]		
Chalcone	3-Phenylindan-1-one	60
2 : 5-Dihydroxyphenyl propenyl ketone	4 : 7-Dihydroxy-3-methylindan-1-one	90
β-Benzoylacrylic acid [4]	1-Ketoindane-3-carboxylic acid	1
β-2-Naphthoylacrylic acid [5]	1-Keto-4 : 5-benzindane-3-carboxylic acid	30

[1] Johnson, "Organic Reactions," Wiley, New York, 1944, Vol. II, p. 114. [2] Blatt, *op. cit.*, 1942, Vol. I, p. 342. [3] Auwers and Risse, *Annalen*, 1933, **502**, 282. [4] Cf. Baddeley, Holt, and Makar, *J.*, 1952, 3289. [5] Cf. Baddeley, Holt, Makar, and Ivinson, *J.*, 1952, 3605.

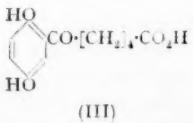
has been extended to glutaric acid to give the diketones (I) and (II) (a detailed study of these compounds will be reported later), but the only identifiable product obtained from the reaction with adipic acid was a little of the keto-acid (III).



(I)



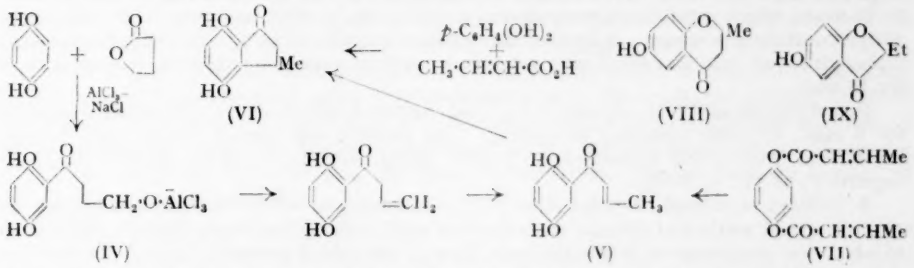
(II)



(III)

The use of γ-lactones in Friedel–Crafts reactions for the preparation of γ-arylbutyric acids was first reported by Eijkmann (*Chem. Weekblad*, 1904, **1**, 421 *et seq.*). Later, Mosby (*J. Amer. Chem. Soc.*, 1952, **74**, 2564) observed the additional formation of tetralones when the reaction time was prolonged, and satisfactory yields of tetralones have been obtained by using excess of aluminium chloride (Arnold, Buckley, and Richter, *ibid.*, 1947, **69**, 2322; Truce and Olson, *ibid.*, 1952, **74**, 4721). We therefore expected no difficulty in preparing 5 : 8-dihydroxytetralone by condensing quinol with γ-butyrolactone in an aluminium chloride–sodium chloride melt, but in fact the product obtained, although

very similar in physical and chemical properties, was the isomeric ketone 4 : 7-dihydroxy-3-methylindanone (VI). It gave a positive reaction with Brady's reagent, a transient blue-green ferric colour, and a yellow alkaline solution [like all the quinol derivatives in section (*c*) of the Table], and formed a diacetate. The lactone ring can open in two ways: (*a*) to form a carbonium ion on the γ-carbon atom, subsequent reaction giving a γ-arylbutyric acid, and (*b*) to form a carbonium ion on the carbonyl carbon atom which gives



rise to the intermediate ketone (IV) and thence by elimination of the alcoholic group and shift of the double bond to form (V) and then (VI). In support of this we also obtained (VI) by cyclisation of 2 : 5-dihydroxyphenyl propenyl ketone (V), by a Fries rearrangement of quinol dicrotonate (VII), and by direct condensation of quinol with crotonic acid. Since the indanone forms a diacetate, the alternative monohydroxychromanone (VIII) and, less probable, coumaranone (IX) structures are eliminated (cf. von Auwers, *Annalen*, 1920, **421**, 1, and other papers). Valerolactone gave the ethyl homologue of (VI) but we could only isolate traces of 1 : 4-dihydroxyanthrone from the reaction between phthalide and quinol (formation of a five-membered ring is impossible in this case).

Experimental

General Procedure.—A mixture of anhydrous aluminium chloride (10 g.) and sodium chloride (2 g.) is melted in a beaker (100 c.c.) by direct heating over a flame, and stirred with a thermometer. The aromatic acid or ester (2 g.) is added at 140°, and the temperature raised rapidly to 180° and kept at 180—200° for 2 min. The mixture is then cooled, decomposed with ice and hydrochloric acid, and worked up in the usual way. In cases where the product is chelated (especially quinol derivatives) it may be necessary to heat the hydrochloric acid mixture to the boil to decompose the complex. In condensation reactions involving two components the amount of aluminium chloride used is five times the combined weights of the two components, which are added as an intimate mixture to the melt. On a larger scale, addition of the organic material must be made gradually to avoid excessive frothing.

δ-(2 : 5-*Dihydroxybenzoyl*)*valeric acid* (III) formed pale yellow leaflets, m. p. 130° (from water) (Found: C, 60·5; H, 5·9. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·8%); its 2 : 4-*dinitrophenylhydrazone* formed orange plates, m. p. 194° (from alcohol) (Found: N, 13·3. $C_{18}H_{16}O_8N_4$ requires N, 13·4%).

4-*Bromo*-2′ : 5′-*dihydroxybenzophenone* formed light yellow needles, m. p. 153° (from benzene–light petroleum) (Found: C, 53·2; H, 3·2. $C_{13}H_9O_3Br$ requires C, 53·25; H, 3·1%); its 2 : 4-*dinitrophenylhydrazone* formed orange-red plates, m. p. 314° (decomp.) (from glacial acetic acid) (Found: N, 11·8. $C_{19}H_{13}O_6N_4Br$ requires N, 11·8%).

1′ : 4′-*Dihydroxy*-1 : 2-*benzo*cyclo*heptene*-3 : 7-*dione* (I).—This *dione* crystallises from light petroleum (b. p. 100—120°) in bright red needles and sublimes *in vacuo* as yellow crystals, m. p. 149° (Found: C, 64·05; H, 4·85. $C_{11}H_{10}O_4$ requires C, 64·05; H, 4·85%). The *diacetate* formed plates, m. p. 170° (from aqueous acetic acid) (Found: C, 62·2; H, 4·85. $C_{15}H_{14}O_6$ requires C, 62·05; H, 4·85%). The *dimethyl ether*, prepared by refluxing with methyl sulphate–acetone–potassium carbonate for 2 hr., crystallised from light petroleum in plates, m. p. 148°, soluble in concentrated hydrochloric acid (Found: C, 67·05; H, 6·05. $C_{13}H_{14}O_4$ requires C, 66·65; H, 6·0%). The p-*nitrophenylhydrazone* formed orange crystals, m. p. 218° (from aqueous alcohol) (Found: N, 12·4. $C_{17}H_{15}O_5N_3$ requires N, 12·3%).

1′ : 4′-*Dihydroxynaphtho*(2′ : 3′-1 : 2)cyclo*heptene*-3 : 7-*dione* (II) formed yellow rosettes, m. p. 121° (from light petroleum) (Found: C, 70·45; H, 4·7. $C_{15}H_{12}O_4$ requires C, 70·3; H,

4·7%); its *dimethyl ether* crystallised from aqueous methanol in plates, m. p. 124° (Found: C, 71·5; H, 5·85. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·65%).

1-*Keto*-2-*phenylindane*-3-*carboxylic Acid*.—This crystallised from water as the *monohydrate*, needles, m. p. 116° Found: C, 70·95; H, 5·16. $C_{16}H_{12}O_3,H_2O$ requires C, 71·1; H, 5·2%). (It was first obtained by Dr. M. B. Watson by monocyclisation of αβ-diphenylsuccinic acid with sulphuric acid; personal communication.) When the keto-acid was heated with concentrated sulphuric acid at 135° for 2 min. it cyclised to form 4*b* : 5 : 9*b* : 10-tetrahydroindeno(2 : 1*a*)indene-5 : 10-dione, which crystallised from alcohol in plates, m. p. 205°, undepressed by admixture with an authentic specimen. A little of this diketone was formed along with the keto-acid when diphenylsuccinic acid was fused with a larger amount of aluminium chloride–sodium chloride for 10 mins.

Quinol Dicrotonate (VII).—Quinol (1·1 g.) and crotonoyl chloride (5 g.) were refluxed together for 3 min. Crystals separated on cooling. The mixture was poured on ice, and the *ester* crystallised from alcohol in needles, m. p. 113° (94%) (Found: C, 68·15; H, 5·7. $C_{14}H_{14}O_4$ requires C, 68·25; H, 5·7%).

2 : 5-*Dihydroxyphenyl Propenyl Ketone* (V).—A suspension of 2 : 5-dihydroxyacetophenone (2 g.) in glacial acetic acid (40 c.c.) was saturated at 0° with dry hydrogen chloride, the passage of which was continued while acetaldehyde (20 c.c.) was added gradually (3 hr.). After 6 hr. the red solution was poured on ice. Next day, the dark viscous oil which had separated was washed repeatedly with water, taken up in chloroform, and then extracted with aqueous potassium hydroxide. The alkaline extract was acidified and again extracted with chloroform, and the latter dried ($CaCl_2$) and evaporated. The residue was sublimed at 175°/10 mm., and the sublimed *ketone* recrystallised from light petroleum (charcoal) in pale yellow needles, m. p. 154·5° (0·1 g.) (Found: C, 67·45; H, 5·8. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·65%).

4 : 7-*Dihydroxy*-3-*methylindan*-1-*one* (VI).—This *ketone* was obtained by the four methods indicated in the Table. It crystallised from light petroleum in clusters of pale yellow plates, m. p. 182—183° (Found: C, 67·45; H, 5·6. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·65%). The *diacetate* crystallised from light petroleum (b. p. 50—60°) in plates, m. p. 75° (Found: C, 63·95; H, 5·25. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%).

3-*Ethyl*-4 : 7-*dihydroxyindan*-1-*one* formed lemon-yellow needles, m. p. 199° (Found: C, 68·55; H, 6·25. $C_{11}H_{12}O_3$ requires C, 68·75; H, 6·3%), and its *diacetate* crystallised in needles, m. p. 102° (from alcohol) (Found: C, 65·15; H, 5·9. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%).

Some of the analyses are by Miss M. A. Buchanan. One of us (A. J. S. S.) thanks the Carnegie Trust for the Universities of Scotland for a scholarship.

The University, Old Aberdeen, Scotland. [*Received, March 2nd,* 1953.]

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490. meta-*Interactions and Inductive Effects in Heterocyclic Systems.*

By D. A. Brown and M. J. S. Dewar.

The apparently anomalous behaviour of β-picoline, and of certain *meta*-substituted benzene derivatives, has been examined theoretically. Two possible explanations have been considered. The first, which postulates a direct *meta*-interaction in aromatic systems, has proved unsatisfactory. The second, based on the conception of an inductoelectromeric effect by which abnormally electronegative carbon atoms exert appreciable electromeric effects, provides a satisfactory explanation of the above anomalies. A general theoretical explanation of the absence of *meta*-interaction effects, based on perturbation theory, is given in the Appendix.

It is well known that α- and γ-picoline differ from the β-isomer in undergoing a number of typical prototropic reactions, for instance, base-catalysed condensations with aldehydes; and this difference is believed to be due to the electromeric electrophilic effect of the annular nitrogen atom. Recently, however, Brown and Murphey (*J. Amer. Chem. Soc.*, 1951, **73**, 3308) have observed that the prototropic reactivity of β-picoline, while less than that of its isomers, is nevertheless very much greater than that of toluene; for β-picoline is readily

alkylated by alkyl halides and sodamide in liquid ammonia, conditions under which toluene does not react at all. A similar anomaly was observed by Bevan and Bye (*Chem. and Ind.*, 1952, 981) in the methanolysis of 1-fluoro-3 : 5-dinitrobenzene, the rate of which is similar to that of the methanolysis of *p*-fluoronitrobenzene under similar conditions; here again the electromeric effect of the nitro-group is apparently transferred to the *meta*-position in a six-membered aromatic ring. Brown and Murphey (*loc. cit.*) suggested that the β-picolinyl anion (I) might be stabilized by contributions from the *meta*-quinonoid structure (II). A recent investigation into the relation between the resonance and the molecular orbital theory (M.O.) (Dewar and Longuet-Higgins, *Proc. Roy. Soc.*, 1952, *A*, **214**, 482) implies that the M.O. parallel of this suggestion would be that (I) is stabilized by direct interaction between pairs of *meta*-carbon atoms, the resonance integral between them being appreciable. In the usual M.O. treatment, which leads to the same conclusions as the classical or resonance theory, resonance integrals between non-adjacent atoms are neglected; according to Brown and Murphey, the new effect implies that the neglect of such integrals is not justifiable.

(I) (II) (III) (IV)

An alternative explanation was given by Dewar (*J. Amer. Chem. Soc.*, 1952, **74**, 3357). The polarity of the C–N σ-bonds in pyridine should raise the electron affinity of the α-carbon atoms, and these electronegative carbon atoms should then activate the β-methyl to prototropy. Such an activation would be due to the electromeric effect of two electronegative atoms in the usual (*o* : *p*) relations to the methyl; since the activating atoms owe their electronegativity to an inductive effect, the overall effect might be termed " inducto-electromeric." In resonance terminology, the stabilization of (I) is here ascribed to the importance of unexcited structures (III, IV) in which the negative charge resides on abnormally electronegative carbon atoms. A theoretical investigation of *o* : *p*-ratios in substitution of benzene derivatives (Dewar, *J.*, 1949, 463) had already shown that this effect must be important, and as an explanation of a novel phenomenon it has the attraction of involving only accepted concepts.

The relative importance of these two possible types of phenomenon have now been studied theoretically.

Method.—Energy levels and charge distributions were calculated for benzene and pyridine by standard L.C.A.O. techniques with and without inclusion of resonance integrals between *meta*-atoms. From these, energy levels and charge distributions were calculated for the benzyl anion by the L.C.M.O. modification of the usual L.C.A.O. method (Dewar, *Proc. Camb. Phil. Soc.*, 1948, **45**, 638). This procedure greatly reduces the labour involved in such calculations. Several parameters were required in addition to the usual C–C resonance integral. The ratio of the C–C resonance integrals between adjacent (1 : 2) and *meta* (1 : 3) atoms in the ring was taken to be 10; the ratio of the corresponding overlap integrals is about 6 (Slater, *J. Chem. Phys.*, 1949, **17**, 1248), and the ratios of the resonance and overlap integrals should be similar. The parameters involving the N atom followed those recommended by Dewar (*J.*, 1949, 463; 1950, 2329) :

Resonance integral of CN bond	= resonance integral for similar CC bond
Coulomb term for nitrogen	= β
Coulomb term for carbon adjacent to nitrogen	= $0{\cdot}4\beta$
Coulomb term for carbon separated by one atom from nitrogen	= $0{\cdot}1\beta$

Approximate charge distributions were also calculated for a number of larger heterocyclic systems by the perturbation method of Coulson and Longuet-Higgins (*J.*, 1949, 971), the values indicated above being used for the various Coulomb integrals.

Overlap was neglected, since its inclusion is known to make no appreciable difference in chemical applications of the M.O. method.

Results and Discussion.—(1) *Energy levels.* Table 1 shows calculated energies for M.O.'s of benzene, benzyl, and pyridine, both with and without inclusion of *meta*-inter-

actions (*i.e.*, of resonance integrals between *meta*-positions in the ring, and between the methylene group and *ortho*-positions in benzyl). The last row shows the calculated total π-electron energies for these molecules, the three values for benzyl corresponding to the cation, radical, and anion respectively. Notice that the total energies of the even systems, and of the odd radical, are virtually unchanged by *meta*-interactions although the individual

TABLE 1.

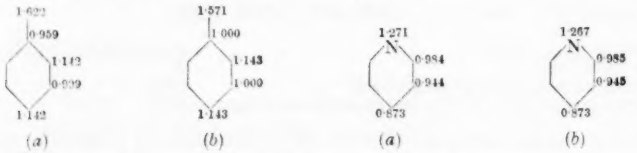
	Benzene		Benzyl		Pyridine	
	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)
Energy levels in units of β (*a*) with and (*b*) without *meta*-interaction	+1·800	+2·000	+1·880	+2·101	+1·573	+1·748
	+1·100	+1·000	+1·311	+1·260	+0·861	+0·761
	+1·100	+1·000	+1·100	+1·000	+0·628	+0·552
	−0·900	−1·000	+0·143	0·000	−1·161	−1·261
	−0·900	−1·000	−0·900	−1·000	−1·282	−1·358
	−1·800	−2·000	−1·210	−1·260	−2·619	−2·443
	—	—	−2·324	−2·101	—	—
Total π-electron energy $\times \beta^{-1}$	8·00	8·00	8·87	8·72	10·12	10·12
	—	—	8·73	8·72	—	—
	—	—	8·68	8·72	—	—

levels alter somewhat; it can be shown (see Appendix) that this is true in general for neutral alternant systems, to a first approximation, and there is therefore probably no need to consider *meta*-interactions when calculating their energies; particularly since the calculations reported here suggest that the higher-order perturbations are very small. Notice also that the " non-bonding " M.O. of benzyl becomes antibonding when *meta*-interactions are included; this result again can be shown to hold quite generally (see Appendix) and would imply that the resonance energies of a related set of odd alternant systems should fall in the order cation>radical>anion if *meta*-interactions are important. (In the absence of *meta*-interactions all three energies are of course equal.) However, the application of the simple M.O. method to such ions involves assumptions of dubious validity (Coulson and Dewar, *Discuss Faraday Soc.*, **1947**, **2**, 54) and too much weight should not be attached to this prediction. Experimental data are lacking.

(2) *Charge densities.* The total π-electron charge distributions in the benzyl anion and in pyridine with and without *meta*-interaction are shown in Fig. 1; the charge distribution in benzene, and indeed the molecular orbitals themselves, are quite unchanged by *meta*-interaction since they are determined rigorously by the symmetry of the molecule.

It will be evident from Fig. 1 that the charge densities are virtually unaltered by *meta*-interactions, except for the methylene group and the carbon atom adjacent to it in the benzyl anion. This result is perhaps unexpected since it can easily be shown that the bond–atom polarizabilities in alternant hydrocarbons vanish only for bonds formed between atoms of opposite parity (see Appendix). A more detailed investigation may show that the change in charge density depends on the environment of the atom; comparison of Fig. 1(*a*) and 1(*b*) suggests that the charges at doubly connected atoms may prove to be

FIG. 1. *Charge distributions in the benzyl anion and in pyridine* (a) *with and* (b) *without* meta-*interactions.*



virtually unaffected by *meta*-interaction, while those at singly connected atoms may be raised and those at triply connected atoms lowered. For the present purpose it is sufficient to know that the charge density at the *meta*-position in the benzyl anion is virtually unchanged by *meta*-interactions and therefore almost identical with the charge density at a *meta*-carbon atom in toluene.

Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1947, *A*, **191**, 39) showed that the change in π-electron energy on replacement of a carbon atom in a mesomeric system by a hetero-atom is given approximately by $q\alpha$, where q is the π-electron density at that position in the isoconjugate hydrocarbon and α is the coulomb term of the hetero-atom, provided that the substitution alters none of the bond resonance integrals, as is probably the case for nitrogen. If then the charge density at the *meta*-position in the benzyl anion is approximately the same as in the *meta*-position of toluene, the π-electron energy of each will be altered equally if that carbon atom is replaced by nitrogen. Such a replacement would then leave the relative energies of toluene and its conjugate base ($Ph{\cdot}CH_2^-$) unaltered, and so β-picoline would resemble toluene in its prototropic reactivity. The greater prototropic reactivity of β-picoline cannot therefore be ascribed to *meta*-interactions as Brown and Murphey suggested.

The alternative explanation, in terms of the inductoelectromeric effect, does account for the observed facts. The energy levels of the three picolinyl anions, with neglect of *meta*-interaction, are listed in Table 2; and the differences (ΔE) in total π-electron energy

TABLE 2. *Energy levels of the picolinyl ions, in units of* β.

α-Picolinyl	β-Picolinyl	γ-Picolinyl	α-Picolinyl	β-Picolinyl	γ-Picolinyl
−0·1784	−0·1140	−0·1797	−1·470	−1·576	−1·616
−1·356	−1·307	−1·261	−2·535	−2·484	−2·472

between toluene and the three picolines on the one hand, and their conjugate anions on the other, are given in Table 3. Since prototropic activity should be greater the greater ΔE, it is evident that β-picoline should show a reactivity intermediate between that of toluene on the one hand, and that of α- or γ-picoline on the other.

TABLE 3. *Total π-electron energies of* $R{\cdot}CH_3$ *and* $R{\cdot}CH_2^-$, *and the differences between them, in units of* β.

R =	Phenyl	β-Pyridyl	α-Pyridyl	γ-Pyridyl
$E_{R\cdot CH_2^-}$	8·72	10·96	11·08	11·05
$E_{R\cdot CH_3}$	8·00	10·12	10·12	10·12
ΔE	0·72	0·84	0·96	0·93

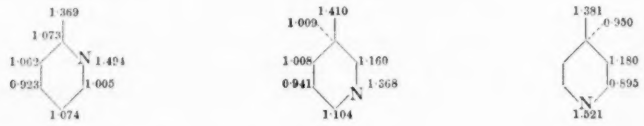
The unusual acidity of β-picoline should therefore be ascribed to the inductoelectromeric effect rather than to *meta*-interactions of the type considered by Brown and Murphey; and this, together with the results obtained earlier (Dewar, *loc. cit.*), suggests strongly that the increase in electronegativity of carbon atoms in heterocyclic systems, due to the inductive effect of the hetero-atoms, must be taken explicitly into account in any theoretical treatment. Note that the inductive effect in question is one operating on the σ-bonds of a molecule; the polarization of the π-electrons may also lead to changes in electronegativity of carbon atoms, but when explicit allowance is made for them (cf. Wheland and Mann, *J. Chem. Phys.*, 1949, **17**, 264) the charge distributions show little qualitative change, the magnitudes of the net charges being reduced more or less proportionately. Consequently, the π-polarizations can probably be absorbed into the empirical parameters used in the simple M.O. treatment.

A further argument for the importance of the inductoelectromeric effect is provided by the basic strengths of the three picolines. The precise mode of action of the methyl group in such compounds is uncertain, but since the effect is undoubtedly nucleophilic, the charge densities on the nitrogen atoms of the picolines should run parallel to those on the nitrogen atoms of the conjugate anions. The charge densities in these anions (with neglect of *meta*-interaction) are listed in Fig. 2. The basic strengths of the picolines do in fact run parallel to the calculated charge densities on nitrogen in these ions (*i.e.*, $\gamma > \alpha \gg \beta$; the observed pK_a are 6·03, 5·94, and 5·66, respectively; Herrington, *Discuss. Faraday Soc.*, 1950, **9**, 26).

Longuet-Higgins (*J.*, 1949, 971) used a perturbation method to calculate the charge distributions in heterocyclic compounds from those in the isoconjugate hydrocarbons.

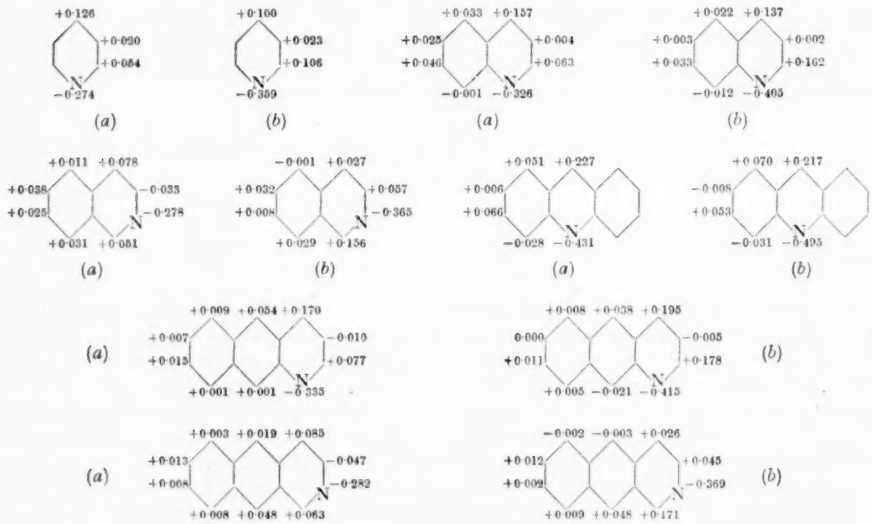
The calculations involved two parameters—the coulomb term of nitrogen, and the allowance for the inductive effect of nitrogen. We think that his value (2β) for the former was too large, and for the latter (factor 1/8) too low. We have accordingly repeated the calculations with our values for the parameters, and the results, in terms of net charge at the various

FIG. 2.



positions, are compared with his in Fig. 3. The two sets of values agree quite well, a satisfactory conclusion in view of the uncertainty in the choice of parameters. It should in any case be emphasised that calculations of charge density by the simple M.O. method cannot be expected to have more than a qualitative significance in view of the known errors

FIG. 3. *Distributions of net charge in heterocyclic compounds calculated* (a) *by us and* (b) *by Longuet-Higgins.*



introduced in the treatment of systems containing hetero-atoms. Charges and charge densities have nevertheless been given throughout to three places of decimals, since their qualitative interrelations should be significant and since they may be of use in other connexions.

(3) *Strengths of heterocyclic bases.* The basic strengths of heterocyclic bases can be related, as Coulson and Longuet-Higgins (*loc. cit.*) showed, to the charge distributions in them. These authors assumed, however, that the determining factor was the change in the coulomb term of the annular nitrogen atom on salt formation; however, the σ-inductive effect will also lead to a change in the coulomb terms of adjacent carbon atoms, presumably proportional to the change in the coulomb term of nitrogen. These being included, the relation between the acid dissociation constant of the acid conjugate to the base becomes:

$$C - 2{\cdot}303\boldsymbol{R}T\ \mathrm{p}K_a = \Delta\alpha\{q_N + 0{\cdot}4\Sigma q_\alpha + 0{\cdot}1\Sigma q_\beta\} \equiv \mathrm{f}(q)\Delta\alpha \quad . \quad . \quad . \quad (1)$$

where q_N is the charge density at the nitrogen atoms, q_α that at carbon atoms α to nitrogen, and q_β that at carbon atoms β to nitrogen. The acid dissociation constants of five of the bases are given in Table 4. It will be seen that the relation of q to pK_a is far from linear; a similar discrepancy had already been noticed by Coulson and Longuet-Higgins, using their original relation between pK_a and q_N. Dyatkina (*Doklady Akad. Nauk, U.S.S.R.*, 1948, **59**, 517) suggested that it might be due to a change in the CN resonance

TABLE 4.

Compound	f(q)	pK_a †	Compound	f(q)	pK_a †	Compound	f(q)	pK_a †
Pyridine	1·227	5·23	Quinoline	1·312	4·94	Acridine ...	1·434	5·60
*iso*Quinoline...	1·263	5·33	6 : 7-Benzoquinoline	1·321	5·05			

† Albert, Goldacre, and Phillips, *J.*, 1948, 2240.

integrals accompanying salt formation; but it seems unlikely that this second-order effect could be appreciable, let alone comparable with the main effect given by equation (1). Another possible explanation would be that the second-order terms, due to the change in charge distribution during salt formation, are appreciable; the main second-order term $\Delta E'$ is given by

$$\Delta E' = \tfrac{1}{2}\pi_{NN}(\Delta\alpha)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when π_{NN} is the self-polarizability of the nitrogen. Since $\Delta\alpha$ is negative, it is easily seen that ΔE should be negative but $\Delta E'$ positive; since the self-polarizability in naphthalene is greater in the α- than in the β-position, this effect should reduce the basicity of quinoline in comparison with that of *iso*quinoline. The observed anomaly is in this direction.

(4) *Dipole moments.* The M.O. method can also be used in principle to estimate dipole moments of conjugated molecules, but the results of such calculations are invariably unsatisfactory in a quantitative sense. This discrepancy cannot be ascribed to the inductoelectromeric effect, as the results in Table 5 show: not only do the calculated and

TABLE 5. *Comparison of calculated and observed dipole moments.*

Compound	Mesomeric moment, in D : calc.	obs.
Pyridine	2·33	0·91
Quinoline	3·40	0·84
Acridine	4·90	0·65

observed mesomeric moments differ greatly, but they also show opposite variations with changes in structure. (The observed mesomeric moments were calculated from the observed dipole moments by subtracting 1·3 D, as recommended by Coulson and Longuet-Higgins, *loc. cit.*)

Conclusions.—It appears that *meta*-interactions can probably be neglected in most connexions, their effect being negligible; but that the σ-inductive effect of hetero-atoms must nearly always be taken into account. With inclusion of this inductoelectromeric effect, the M.O. method seems to give a reasonably satisfactory account of resonance energies in heterocyclic systems; but the calculations of charge density and quantities derived from it are still very disappointing. This is not surprising, since it is well known that the energy of a system given by any variation method is relatively insensitive to variation in the parameters of the trial eigenfunction, and that such methods, of which the M.O. method is one, commonly give much better approximations to the energies of systems than to their eigenfunctions.

Appendix.

(1) *Inclusion of* meta-*interactions does not, to a first approximation, alter the total energy of a neutral alternant system.* Consider, first, an even alternant hydrocarbon. The energy

levels appear in pairs, of energy $\pm E_m$ (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193), the corresponding M.O.'s ψ_{m^+}, ψ_{m^-} being given by

$$\psi_{m^+} = \overset{*}{\sum_r} a_{mr}\phi_r + \overset{0}{\sum_t} a_{mt}\phi_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\psi_{m^-} = \overset{*}{\sum_r} a_{mr}\phi_r - \overset{0}{\sum_t} a_{mt}\phi_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ϕ_r is the atomic orbital of atom r and $\overset{*}{\Sigma}$, $\overset{0}{\Sigma}$ imply summation over starred and unstarred atomic orbitals respectively. Then the corrections for *meta*-interactions, ΔE_{m^+}, ΔE_{m^-}, are given approximately by first-order perturbation theory as

$$\left.\begin{aligned}\Delta E_{m^+} &= -2\beta'\left\{\overset{*}{\sum_{r<d}}\overset{*}{\sum} a_{mr}a_{md} + \overset{0}{\sum_{t<u}}\overset{0}{\sum} a_{mt}a_{mu}\right\}\\ \Delta E_{m^-} &= -2\beta'\left\{\overset{*}{\sum_{r<d}}\overset{*}{\sum} a_{mr}a_{md} + \overset{0}{\sum_{t<u}}\overset{0}{\sum}(-a_{mt})(-a_{mu})\right\}\end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

where β' is the resonance integral between *meta*-atoms. Hence

$$\Delta E_{m^+} = \Delta E_{m^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The total energy change $E_{\text{occ.}}$ for all the occupied molecular orbitals is given by

$$\left.\begin{aligned}\Delta E &= 2\sum_m \Delta E_{m^+}\\ &= \sum_m \Delta E_{m^+} + \sum_m \Delta E_{m^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)\end{aligned}\right.$$

So ΔE is equal to the sum of the corrections to all the energy levels, bonding and antibonding. But the complete secular determinant is of the form

$$\begin{vmatrix} W & \beta_{12} & \beta_{13} & \cdot & \cdot & \cdot & \beta_{1n} \\ \beta_{21} & W & \beta_{23} & \cdot & \cdot & \cdot & \beta_{2n} \\ \beta_{31} & \beta_{32} & W & \cdot & \cdot & \cdot & \beta_{3n} \\ \cdot & \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & \cdot & & & & \cdot \\ \cdot & \cdot & \cdot & & & & \cdot \\ \beta_{n1} & \beta_{n2} & \beta_{n3} & \cdot & \cdot & \cdot & W \end{vmatrix} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where β_{vs} is the resonance integral between atoms v and s and no such integrals are neglected. Expanding this determinant, one obtains an equation for W in which the coefficient of W^{n-1} vanishes. Hence the sum of the roots is zero. Therefore the sum of all the energy levels vanishes; since this is true whatever the values of the β_{vs}, it must be true both for the set of levels found with neglect of *meta*-interaction, and for the set found including *meta*-interaction. Consequently, the sum of all the corrections for *meta*-interaction vanishes, and so therefore does ΔE [equation (6)]. This proves the theorem for even alternant hydrocarbons. The proof for odd alternant hydrocarbons radicals is precisely similar; the equation corresponding to equation (6) is then

$$\left.\begin{aligned}\Delta E &= 2\sum_{m\neq 0} \Delta E_{m^+} + \Delta E_0\\ &= \sum_{m\neq 0} \Delta E_{m^+} + \Delta E_0 + \sum_{m\neq 0} \Delta E_{m^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)\end{aligned}\right.$$

where ΔE_0 is the energy of the singly occupied (" non-bonding ") molecular orbital. The last line of (8) shows that ΔE is again equal to the sum of the corrections to all the molecular orbitals for *meta*-interaction, and the same argument shows that this sum must vanish.

These results can at once be extended to isoconjugate heterocyclic systems since, to a first approximation, the charge densities at the individual atoms are unaffected by changes

in their coulomb terms (cf. Coulson and Longuet-Higgins, *loc. cit.*; the changes in charge density are second-order effects).

(2) *Inclusion of* meta-*interactions in an odd alternant hydrocarbon raises the energy of the non-bonding molecular orbital (and so makes it antibonding).* Let the carbon atoms, at most three in number, attached to an inactive atom r, be s, t, u. With the usual assumption that resonance integrals between adjacent carbon atoms are similar ($=\beta$), the non-bonding molecular orbital coefficients a_{0s}, a_{0t}, a_{0u} at atoms s, t, u are related (Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265) by

$$a_{0s} + a_{0t} + a_{0u} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

To a first approximation, *meta*-interactions in this molecular orbital will occur only between active atoms, since the molecular orbital will be unchanged to a first approximation. The total energy E_{stu} for interactions between atom s, t, u, will then be given by

$$E_{stu} = -2\beta'(a_{0s}a_{0t} + a_{0t}a_{0u} + a_{0u}a_{0s}) \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where β' is the resonance integral between *meta*-carbon atoms. Combining equations (9) and (10), we have

$$\begin{aligned} E_{stu} &= -2\beta'\{a_{0s}a_{0t} - (a_{0s} + a_{0u})(a_{0s} + a_{0t})\} \\ &= 2\beta'\{a_{0s}^2 + a_{0s}a_{0t} + a_{0t}^2\} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11) \end{aligned}$$

Since the whole change in the energy of the molecular orbital is a sum of terms similar to E_{stu}, and since these are all positive, the *meta*-interactions must raise the energy of the molecular orbital.

(3) *Charge distribution in alternant hydrocarbons should be altered by* meta-*interactions.* The charge density at atom r is related to the resonance integral β_{st} of the bond s–t by the expression $\pi_{r,st} = \partial q_r/\partial\beta_{st}$ (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1948, **191**, *A*, 39) or equivalently $\delta q_r = \pi_{r,st}\delta\beta_{st}$. Coulson and Longuet-Higgins showed by a perturbation treatment that

$$\pi_{r,st} = 4\sum_{j=1}^{m}\sum_{k=m+1}^{n}\frac{a_{jr}\,a_{kr}\,(a_{js}a_{kt} + a_{jt}a_{ks})}{\varepsilon_j - \varepsilon_k}$$

there being m occupied levels, and ε_i being the energy of the ith molecular orbital.

Consider a pair of levels ε_u and ε_v in an alternant hydrocarbon. Two cases arise:

(*a*) If atoms s and t are of opposite parity, so that $c_{sj} = -c_{tj}$, then on summation over occupied and unoccupied levels the sign of the numerator is invariant whilst that of the denominator changes. Hence, on summing over all such pairs, the value of $\pi_{r,st}$ is seen to be zero.

(*b*) If atoms s and t are of same parity, both the numerator and denominator change sign, and hence $\pi_{r,st}$ is no longer zero.

Consequently, changes in the resonance integrals of bonds between atoms of like parity do alter the charge distribution in alternant hydrocarbons, whereas changes in resonance integrals of bonds between atoms of opposite parity leave that charge distribution unchanged to a first approximation (Coulson and Longuet-Higgins, *loc. cit.*). Since *meta*-interactions can be regarded as being due to an increase in resonance integrals of bonds between atoms (*meta*) of like parity from zero to some finite value, they should in general alter the charge distribution.

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491. *The Chemistry of Fungi. Part XVIII.* The Cyclic System of Eburicoic Acid.*

By J. S. E. Holker, A. D. G. Powell, Alexander Robertson, J. J. H. Simes, and R. S. Wright.

From nuclear transformations effected with eburicoic acid it is concluded that this compound contains a cyclic system comprising rings A, B, and C of the lanosterol molecule. The position of the hydroxyl group in ring A has been confirmed by cleavage of the system to a dibasic acid subsequently converted on pyrolysis into a five-membered cyclic ketone. Further, the position of the inert double bond relative to the hydroxyl group in eburicoic acid has been indicated by the conversion of methyl 3-hydroxy-7 : 11-diketoeburicanoate (IX; R = H) into methyl 7 : 11-diketo*iso*eburic-5-enoate (XI) with phosphorus pentachloride according to standard procedure.

Methyl 3-acetoxyeburic-8-enoate is converted into methyl 3-acetoxyeburic-7-enoate (XIII).

Oxidation of methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate gives methyl 3-acetoxy-7 : 11 : 12-triketoeburico-5 : 8-dienoate (XVII). In methyl 3-acetoxy-7 : 11-diketoeburicanoate (IX; R = Ac) only the keto-group in the 7-position is reactive.

As in lanosterol the presence of angular methyl groups at $C_{(10)}$, $C_{(13)}$, and $C_{(14)}$ in eburicoic acid is deduced.

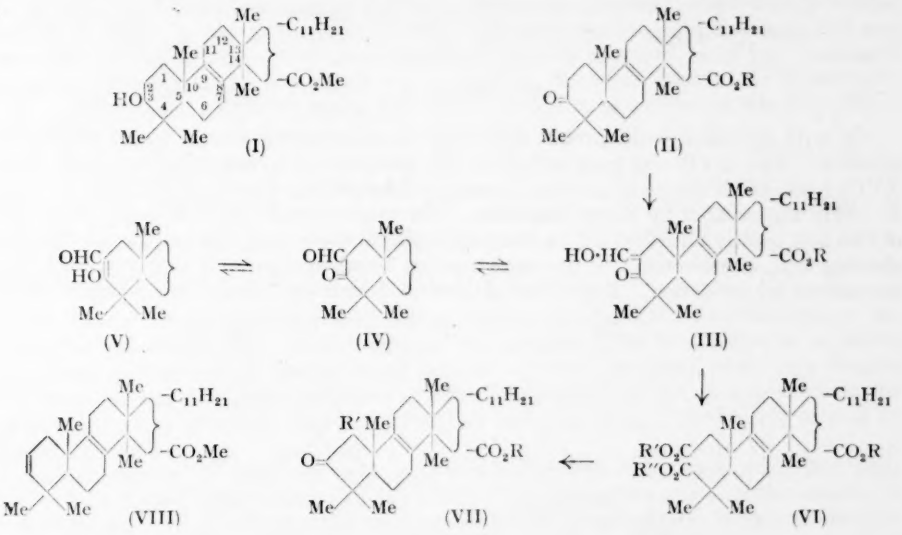
From the behaviour of methyl 3-hydroxyeburic-8-enoate † (dihydroeburicoate) (I) on treatment with phosphorus pentachloride it was suggested in Part XVI (*J.*, 1951, 2346) that the secondary hydroxyl group of eburicoic acid is in a six-membered terminal ring in the α-position to the carbon atom carrying the *gem*-dimethyl group. An examination of the oxidative scission of this ring according to the well-defined standard procedure has now provided evidence in confirmation of this view. Thus, condensation of methyl 3-ketoeburic-8-enoate (II; R = Me) with ethyl formate by sodium ethoxide gave a hydroxymethylene derivative (III; R = Me) which on oxidation with alkaline hydrogen peroxide furnished the monomethyl ester (VI; R = Me, R′ = R″ = H) of a tribasic acid. On pyrolysis this ester gave a keto-ester, methyl A-nor-2-ketoeburic-8-enoate (VII; R = Me, R′ = H), which has an infra-red absorption spectrum with a shoulder at 1733 cm.$^{-1}$ characteristic of a five-membered homocyclic ketone; the expected peak is partly masked by the absorption band due to the carbomethoxy-group at 1721 cm.$^{-1}$. Prepared by the pyrolysis of the tribasic acid (VI; R = R′ = R″ = H) the corresponding A-nor-2-ketoeburic-8-enoic acid (VII; R = R′ = H), however, gave an infra-red spectrum with bands at 1705 and 1733 cm.$^{-1}$ due respectively to carboxyl and carbonyl groups where the absorption characteristic of the five-membered cyclic ketone appears as a fully resolved peak.

In the absence of free mineral acid during the isolation process, the product from the condensation of the ethyl formate and the ester (II; R = Me) had m. p. 121—123° ($\lambda_{max.}$ 290 mμ, log ε 3·90) and with alcoholic ferric chloride gave instantaneously an intense ferric reaction. On treatment with a trace of hydrochloric acid this compound was converted into an isomeride, m. p. 153° ($\lambda_{max.}$ 275 mμ, log ε 4·02), which slowly developed a colour with alcoholic ferric chloride and, on treatment with alkali, regenerated the compound, m. p. 121—123°. On oxidation both compounds gave the ester (VI; R = Me, R′ = R″ = H). Clearly the product, represented as a formyl derivative by (IV), may also exist in two enolic forms (III) and (V). The structure and relations of the isomerides are being investigated but it may be noted that the intensity of the ultra-violet absorption spectra exhibited indicates the presence of enolic chromophores in both isomerides.

* Part XVII, *J.*, 1953, 1830.

† The relation of the cyclic system in eburicoic acid $C_{31}H_{50}O_3$ to that of lanosterol $C_{30}H_{50}O$ deduced in Part XVII * is clarified by the work described in the present communication. We are, therefore, adopting standard steroid numbering (see formula I) for rings A, B, and C. Where possible systematic nomenclature will now be used in which eburicanoic acid is the parent saturated system.

In keeping with the partial structure (VI; R = R′ = R″ = H) proposed for the tribasic acid formed by scission of (III; R = H) the trimethyl ester (VI; R = R′ = R″ = Me) of this acid is readily hydrolysed with methanolic potassium hydroxide to give a dimethyl ester which, in all probability, has the formula (VI; R = R″ = Me, R′ = H). The primary carbomethoxy-group arising from ring A would be preferentially attacked and under the conditions employed the carbomethoxy-group originally present is not hydrolysed (cf. Part XVI, *loc. cit.*) whilst the tertiary carbomethoxy-group from ring A would be expected to behave similarly. Along with the ester (VI; R = R″ = Me, R′ = H) there is formed methyl A-nor-2-ketoeburic-8-enoate which clearly arises from (VI; R = R′ = R″ = Me) by a Dieckmann condensation with subsequent hydrolysis and decarboxylation of the β-keto-ester (VII; R = Me, R′ = CO_2Me) initially formed.



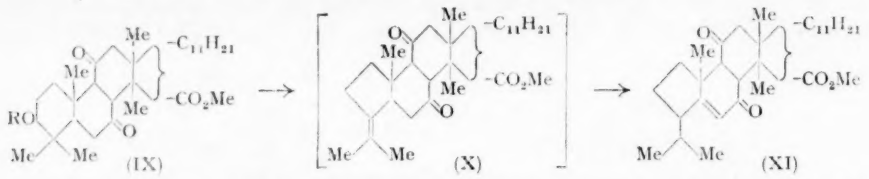
In contrast with the action of phosphorus pentachloride it has been found that on treatment with phosphoryl chloride methyl 3-hydroxyeburic-8-enoate (I) (dihydroeburicoate; Part XVI, *loc. cit.*) is dehydrated to a diene without the simultaneous transformation of ring A. Further, since this compound has an infra-red spectrum with a peak at 733 cm.$^{-1}$ characteristic of the system CHR:CHR (*cis*-form) it appears to be methyl eburico-2 : 8-dienoate (VIII) in agreement with its conversion into methyl eburic-8-enoate (methyl eburicenate; Part XVI) on hydrogenation.

In view of the similarities between the eburicoic acid and the lanosterol–agnosterol series (cf. also Part XVII) the following series of nuclear rearrangements and oxidations were undertaken. The results correspond closely to those observed with the lanosterol nucleus, and indicate clearly that rings A, B, and C of eburicoic acid and of lanosterol are structurally identical (cf. Dorée, McGhie, and Kurzer, *J.*, 1949, 570; Voser, Montavon, Günthard, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1950, **33**, 1893; Cavalla, McGhie, and Pradhan, *J.*, 1951, 3142; Barton, Fawcett, and Thomas, *ibid.*, p. 3147).

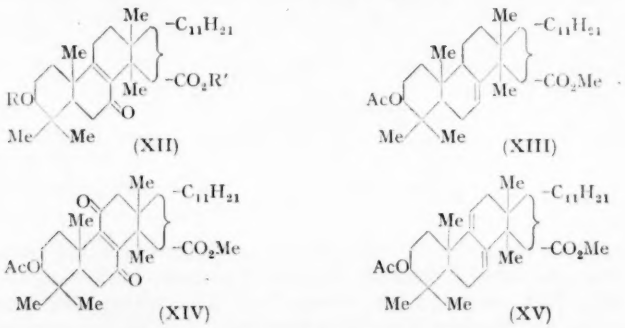
On reduction with zinc and acetic acid methyl 3-hydroxy-7 : 11-diketoeburic-8-enoate (dihydrodiketoeburicoate; Part XVII) gave rise to a saturated diketone, methyl 3-hydroxy-7 : 11-diketoeburicanoate (IX; R = H), which forms only a mono-2 : 4-dinitrophenylhydrazone ($\lambda_{max.}$ 361 mμ, log ε 4·39) indicating that one of the carbonyl groups is sterically hindered, as is the 11-keto-group in the sterol and lanosterol series. On dehydration with phosphorus pentachloride the diketone (IX; R = H) furnished methyl 7 : 11-diketo-*iso*eburic-5-enoate (XI). This conversion presumably arises by retropinacolic arrangement of (IX; R = H) into an intermediate of type (X) which, under acidic conditions is

immediately transformed into (XI), where the double bond initially introduced, *i.e.*, in (X), becomes conjugated with a carbonyl group.

Methyl 7 : 11-diketo*iso*eburic-5-enoate gives only a mono-2 : 4-dinitrophenylhydrazone and from a consideration of the ultra-violet absorption spectrum of this derivative ($\lambda_{max.}$ 387 mμ, log ε 4·42) it is clear that the double bond is in conjugation with the more active carbonyl group which, therefore, is at $C_{(7)}$ in ring B. Hence, by analogy with the corresponding lanosterol derivatives (Barton *et al.*, Cavalla *et al.*, *locc. cit.*), the relation between the hydroxyl group in ring A and the carbonyl group in ring B of (IX) is established and, further, the $C_{(5)}$- and the $C_{(6)}$-atom each carry at least one hydrogen atom.



On mild oxidation with chromic anhydride 3-acetoxyeburic-8-enoic (*O*-acetyldihydroeburicoic; Part XVI) acid gave a mixture (cf. oxidation of *O*-acetyleburicoic acid; Part XVII) from which the main product, 3-acetoxy-7-ketoeburic-8-enoic acid (XII; R = Ac, R′ = H) was isolated by chromatography. The methyl ester (XII; R = Ac, R′ = Me) of this acid readily furnished a 2 : 4-dinitrophenylhydrazone ($\lambda_{max.}$ 390 mμ, log ε 4·47), thus showing that, as expected, it is the more reactive 7-carbonyl group in ring B which is first introduced by oxidation. Reduction of methyl 3-hydroxy-7-ketoeburic-8-enoate (XII;

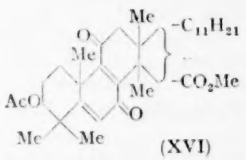


R = H, R′ = Me) by the Wolff–Kishner method followed by successive methylation and acetylation yielded an isomeride of methyl 3-acetoxyeburic-8-enoate in which the double bond is triply substituted (infra-red band at 823 cm.$^{-1}$). Since it has been shown (Lardelli and Jeger, *Helv. Chim. Acta*, 1949, **32**, 1817; Fischer, Lardelli, and Jeger, *ibid.*, 1950, **33**, 1335; 1951, **34**, 1577; Barton, Holness, and Klyne, *J.*, 1949, 2456) that the reduction of αβ-unsaturated ketones by this method is accompanied by the migration of the double bond to the carbon atom originally present in a carbonyl group, clearly this isomeride is methyl 3-acetoxyeburic-7-enoate (XIII).

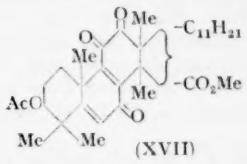
The compound (XIII) is also formed by the action of hydrogen chloride in acetic acid on methyl 3-acetoxyeburic-8-enoate. With a hydrogen atom at $C_{(10)}$ or $C_{(14)}$ it would be expected that under these conditions the double bond would migrate to the more stable $\Delta^{8(14)}$ or Δ^{9}-position and, therefore, the isolation of (XIII) in the absence of other reaction products indicates that $C_{(10)}$ and $C_{(14)}$ are fully substituted and it is suggested that each carries a methyl group. Methyl 3-acetoxyeburic-7-enoate could not be hydrogenated with hydrogen at atmospheric pressure and on oxidation with chromic anhydride gave methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (XIV) (*O*-acetyldihydrodiketoeburicoate, Part XVII), whilst with selenium dioxide it formed the heteroannular diene methyl 3-acetoxyeburico-7 : 9(11)-dienoate (XV) (*O*-acetyldehydrodihydroeburicoate, Part XVII).

On oxidation with selenium dioxide in boiling acetic anhydride methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (XIV) furnished a diketo-diene ($\lambda_{max.}$ 274 mμ, log ε 4·00) along with small amounts of a triketo-diene ($\lambda_{max.}$ 286 mμ, log ε 4·02) which, however, was obtained in better yield when the acetic anhydride was replaced by nitrobenzene. From a comparison of the ultra-violet absorption spectra of these oxidation products with the corresponding dihydrolanosterol derivatives the diketo-diene appears to be methyl 3-acetoxy-7 : 11-diketoeburico-5 : 8-dienoate (XVI), and the triketo-diene to be methyl 3-acetoxy-7 : 11 : 12-triketoeburico-5 : 8-dienoate (XVII) (Voser *et al.*, and Dorée *et al.*, *locc. cit.*). As with the triketone from lanosterol the failure to extend the conjugated system of (XVII) by further oxidation of this compound may be regarded as indicating that in addition to the *C*-methyl groups at $C_{(10)}$ and $C_{(14)}$ there is also a *C*-methyl group at $C_{(13)}$.

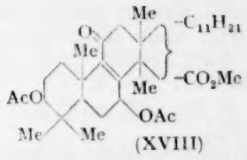
Attempts to oxidise (XIV) at the 8 : 9-double bond were unsuccessful. On reduction by the Meerwein–Ponndorf method this compound gave a product which on acetylation gave a diacetate, failed to form a 2 : 4-dinitrophenylhydrazone, and had $\lambda_{max.}$ 253 and 347—349 mμ (log ε 4·02, 2·74), thus indicating that, as expected, only the 7-carbonyl group was reduced. The acetate of the product is, therefore, methyl 3 : 7-diacetoxy-11-ketoeburic-8-enoate (XVIII) which, like (XIV), could not be oxidised at the Δ^8-position.



(XVI)



(XVII)



(XVIII)

The degradation experiments described are explained satisfactorily on the basis of the partial formulæ employed. On this account, and because of the similarities in the molecular-rotation differences of derivatives of eburicoic acid and lanosterol, where only changes in rings A, B, and C (already described in Part XVII) are involved, it appears that the nuclear system of eburicoic acid is structurally and stereochemically closely related to that of lanosterol.

The conversion of eburicoic acid into eburic-8-en-3-ol (dihydroeburicol) has been achieved by Lahey and Strasser (*J.*, 1951, 873). An alternative route to this alcohol is now described. Prepared from the corresponding acid, 3-acetoxyeburic-8-enoyl chloride was reduced by Rosenmund's method to 3-acetoxyeburic-8-enal, the hydrazone of which was reduced with simultaneous deacetylation by the Wolff–Kishner method to give eburic-8-en-3-ol. When the hydrazone was replaced by the semicarbazone in the latter reaction the alcohol was accompanied by a small amount of an isomeric compound.

Experimental

Specific rotations were measured in chloroform with a 1-dm. tube except where otherwise stated. Ultra-violet absorption spectra were determined in alcohol with a Unicam Spectrophotometer. Infra-red absorption measurements were made with a Grubb Parsons single-beam spectrometer and a paste of the material in "Nujol." Except where stated the light petroleum used had b. p. 60—80°.

Methyl 2-Hydroxymethylene-3-ketoeburic-8-enoate (III; R = Me).—Esterification of 3-ketoeburic-8-enoic acid (eburicenonic acid, Part XVI) with ethereal diazomethane gave the *methyl* ester (II; R = Me) which formed slender needles, m. p. 123—124°, $[\alpha]_D^{20}$ +61° (*c*, 2·0), from methanol (Found: C, 79·7; H, 11·0. $C_{32}H_{52}O_3$ requires C, 79·3; H, 10·7%).

A solution of methyl 3-ketoeburic-8-enoate (0·2 g.) and ethyl formate (0·4 g.) in ether (3·2 ml.) was added slowly to alcoholic sodium ethoxide (0·15 g. of sodium and 3·2 ml. of alcohol), and the cloudy mixture heated under reflux (moisture absent) for ½ hr., kept for 16 hr., and poured on ice and hydrochloric acid. On isolation an ethereal solution of the product was washed repeatedly to remove acid, dried, and evaporated, leaving *methyl 2-hydroxymethylene-3-ketoeburic-8-enoate* which separated from methanol in clusters of needles (0·15 g.), m. p. 121—123°, $[\alpha]_D^{20}$ +110° (*c*, 1·49), giving an instantaneous deep purple ferric reaction in alcohol (Found: C, 77·6; H, 10·3. $C_{33}H_{52}O_4$ requires C, 77·3; H, 10·2%). When the ethereal solution of the

crude product was not completely freed from traces of hydrochloric acid evaporation of the dried solution then gave a compound forming needles, m. p. 153°, $[\alpha]_D^{20}$ +103° (*c*, 1·43) from methanol, which did not give an immediate reaction with alcoholic ferric chloride; the deep purple colour developed during ½ hr. (Found: C, 77·1; H, 10·0%). A mixture of the two compounds melted at about 116°. When a solution of the compound, m. p. 121—123°, in ether containing a trace of hydrogen chloride was kept for 15 min. and then evaporated the residue consisted of the compound, m. p. 153°, which, in turn, on treatment with 10% alcoholic sodium hydroxide for 15 min. regenerated the compound, m. p. 121—123°, provided care was taken in the isolation procedure to remove, from the ethereal solution of the product, traces of hydrochloric acid employed in the neutralisation of the alkaline reaction mixture which had been diluted with ice-water.

Oxidation of Methyl 2-Hydroxymethylene-3-ketoeburic-8-enoate with Hydrogen Peroxide.—Hydrogen peroxide (0·6 ml. of 100-vol.) and 10% aqueous sodium hydroxide were added to methyl 2-hydroxymethylene-3-ketoeburic-8-enoate (0·2 g.), dissolved in alcohol (3 ml.), and the mixture was heated on the steam-bath for 20 min. More 10% aqueous sodium hydroxide (3·3 ml.) and hydrogen peroxide (1·2 ml. of 100-vol.) were then added and next day the reaction mixture was acidified with dilute sulphuric acid and extracted with ether. From the combined ethereal extracts the *monomethyl* ester (VI; R = Me, R′ = R″ = H) of a tricarboxylic acid was isolated with 2N-sodium carbonate and purified from light petroleum containing a trace of alcohol, forming slender needles, m. p. 215—216°, $[\alpha]_D^{20}$ +62° (*c*, 0·72) [Found: C, 72·5; H, 10·0%; equiv. (by potentiometric titration in 50% alcohol), 274. $C_{32}H_{52}O_6$ requires C, 72·2; H, 9·8%; equiv., 266]. With ethereal diazomethane this compound gave the *trimethyl* ester (VI; R = R′ = R″ = Me) which separated from methanol at 0° in feathery needles, m. p. 78°, $[\alpha]_D^{20}$ +19° (*c*, 1·02) (Found: C, 73·2; H, 10·2. $C_{34}H_{56}O_6$ requires C, 72·9; H, 10·0%).

Hydrolysis of the monomethyl ester (1 g.) with boiling diethylene glycol (30 ml.) containing 10% of potassium hydroxide for 3 hr. gave the *tricarboxylic acid* (VI; R = R′ = R″ = H) which was isolated with ether from the cooled hydrolysate after dilution with water (150 ml.) and acidification with 2N-hydrochloric acid. Crystallised from acetic acid, this acid formed small needles, m. p. 278—280° (decomp.), $[\alpha]_D^{20}$ +36° (*c*, 0·97) (Found: C, 72·0; H, 9·6%; equiv., 176. $C_{31}H_{50}O_6$ requires C, 71·8; H, 9·7%; equiv., 173).

Pyrolysis of the Tricarboxylic Acid (VI; R = R′ = R″ = H) *and of its Monomethyl Ester.*—The acid (0·2 g.) was kept at 280—300° in nitrogen for 1 hr. and the product distilled at 210°/0·1 mm., giving A-*nor*-2-*ketoeburic*-8-*enoic acid* (VII; R = R′ = H) which separated from methanol in needles (0·07 g.), m. p. 258°, $[\alpha]_D^{20}$ +98° (*c*, 2·50) (Found: C, 78·9; H, 10·6. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·5%).

Pyrolysis of the monomethyl ester (0·13 g.) under the same conditions gave a product which was dissolved in light petroleum (20 ml.) and the solution poured on a column of aluminium oxide. Elution with light petroleum (40 ml.) gave *methyl* A-*nor*-2-*ketoeburic*-8-*enoate* (VII; R = Me, R′ = H) which separated from methanol in needles (0·06 g.), m. p. 185°, $[\alpha]_D^{20}$ +112° (*c*, 1·1; 0·5-dm. micro-tube) (Found: C, 79·2; H, 10·7. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·6%). Prepared by the pyridine method, the *oxime* separated from benzene–light petroleum in slender needles, m. p. 180—184° (Found: N, 2·9. $C_{31}H_{51}O_3N$ requires N, 2·9%).

The ester (VII; R = Me, R′ = H) was also formed by boiling the trimethyl ester (VI; R = R′ = R″ = Me) with 0·5N-alcoholic potassium hydroxide for 48 hr., and isolated with ether from the reaction mixture after dilution with water (100 ml.). The compound formed needles, m. p. and mixed m. p. 180—183°, $[\alpha]_D^{20}$ +118° (*c*, 2·2; 0·5-dm. micro-tube) (Found: C, 79·4; H, 10·6%), and gave the oxime, m. p. 180—184°, undepressed on admixture with an authentic specimen. After the isolation of this ester the residual alkaline liquor was acidified with sulphuric acid, and the precipitated product isolated with ether. Crystallised from methanol, this gave the *dimethyl* ester (VI; R = R″ = Me, R′ = H) which formed aggregates of thick needles, m. p. 150—152°, $[\alpha]_D^{20}$ +29° (*c*, 1·2), from methanol (Found: C, 72·6; H, 10·0%; equiv., 575. $C_{33}H_{54}O_6$ requires C, 72·5; H, 9·9%; equiv., 546). With ethereal diazomethane this compound gave the trimethyl ester, m. p. and mixed m. p. 78°, of the tribasic acid $C_{31}H_{50}O_6$.

Methyl Eburico-2:8-dienoate (VIII).—Phosphoryl chloride (5 ml.) was added slowly to a well-stirred solution of methyl 3-hydroxyeburic-8-enoate (I) (dihydroeburicoate, Part XVI) (3·3 g.) in pyridine (33 ml.), and the warm mixture (80°) heated on the steam-bath for 1½ hr., boiled for 3 min., cooled, and poured on crushed ice and excess of hydrochloric acid. After isolation with ether a solution of the product in light petroleum was poured on a column of

aluminium oxide. Extraction of the oxide with excess of light petroleum gave *methyl eburico-2 : 8-dienoate* which separated from methanol in colourless needles (1 g.), m. p. 154—155°, $[\alpha]_D^{20}$ +105° (*c*, 1·92) (Found: C, 82·3; H, 11·3. $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1%). On hydrogenation in acetic acid at 100°/70 atm. with a platinum catalyst this compound gave methyl eburic-8-enoate in needles, m. p. 102° (Found: C, 81·6; H, 11·3. Calc. for $C_{32}H_{54}O_2$: C, 81·7; H, 11·5%). Thus obtained methyl eburic-8-enoate was identical with a specimen prepared by the hydrogenation of methyl eburico-8 : 24(28)-dienoate (eburicodienate, Part XVI) with hydrogen at atmospheric pressure and a platinum or W5 Raney nickel catalyst. Owing to an error in transcription the m. p. of this dihydro-derivative (methyl eburicenate) was erroneously stated in Part XVI to be 118—119·5°.

Methyl 3-Hydroxy-7 : 11-diketoeburicanoate (IX; R = H).—This compound was prepared by the reduction of methyl 3-hydroxy-7 : 11-diketoeburic-8-enoate (dihydrodiketoeburicoate, Part XVII) (1 g.) with zinc and acetic acid by the method employed for methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (methyl *O*-acetyldihydrodiketoeburicoate, Part XVII) and on purification from methanol formed colourless needles (0·6 g.), which contained solvent of crystallisation and melted at 113—115°, solidified at about 150—153°, and then melted at 176—177°. A solution of the solvated product in much light petroleum was evaporated until saturated and on cooling then deposited *methyl 3-hydroxy-7 : 11-diketoeburicanoate* in needles, m. p. 181—182°, $[\alpha]_D^{21}$ +43° (*c*, 1·31), $\lambda_{max.}$ 295 mμ (log ε 1·80) (Found: C, 74·6; H, 9·9. $C_{32}H_{52}O_5$ requires C, 74·4; H, 10·1%). The 2 : 4-*dinitrophenylhydrazone* separated from alcohol in red needles, m. p. 258—259° (decomp.) (Found: N, 8·2. $C_{38}H_{56}O_8N_4$ requires N, 8·0%). Hydrolysis of the ester with hot alcoholic potassium hydroxide gave an inseparable mixture.

Methyl 7 : 11-Diketoisoeburic-5-enoate (XI).—A mixture of phosphorus pentachloride (2 g.), methyl 3-hydroxy-7 : 11-diketoeburicanoate (0·7 g.), and light petroleum (b. p. 40—60°) (350 ml.) was agitated for 1 hr., filtered, washed with 2N-sodium hydroxide and water, dried, and concentrated to 100 ml. This solution was poured on aluminium oxide (24 × 1·8 cm.), and the column eluted with benzene–light petroleum (1 : 4; 700 ml.), giving *methyl 7 : 11-diketoisoburic-5-enoate* as a colourless resin (0·42 g.) which crystallised from methanol in colourless needles, m. p. 162—163°, $[\alpha]_D^{20}$ +18° (*c*, 2·91; 0·5-dm. micro-tube), $\lambda_{max.}$ 242, 295—296 mμ (log ε 3·87, 2·61) (Found: C, 76·3; H, 10·5. $C_{32}H_{54}O_4$ requires C, 76·4; H, 10·8%). The 2 : 4-*dinitrophenylhydrazone* formed red needles, m. p. 172—175°, from alcohol (Found: N, 7·8. $C_{38}H_{58}O_7N_4$ requires N, 8·2%). Further elution of the column with benzene–light petroleum (1 : 2) and acetone–benzene (1 : 19) gave yellow resins which did not crystallise from solvents.

3-Acetoxy-7-ketoeburic-8-enoic Acid (*O-Acetyldihydroketoeburicoic Acid*) (XII; R = Ac, R′ = H).—3-Acetoxyeburic-8-enoic acid (*O*-acetyldihydroeburicoic acid, Part XVI) (8·5 g.), dissolved in acetic acid (500 ml.), was oxidised with a solution of chromic anhydride (2·8 g.) in acetic acid (100 ml.) and water (20 ml.) at room temperature for 4 days and the product isolated by the method employed for *O*-acetylketoeburicoic acid (Part XVII). From the mixture of ketonic acids *3-acetoxy-7-ketoeburic-8-enoic acid* was isolated by chromatography on neutralised aluminium oxide and purified from dilute alcohol, forming colourless needles (1·1 g.), m. p. 238—240°, $[\alpha]_D^{20}$ +12° (*c*, 2·65), $\lambda_{max.}$ 251 mμ (log ε 3·98) with an inflexion at about 315 mμ (log ε 1·85) (Found: C, 75·2; H, 10·1. $C_{33}H_{52}O_5$ requires C, 75·0; H, 9·9%). The *methyl* ester (XII; R = Ac, R′ = Me) formed needles, m. p. 164—165°, $[\alpha]_D^{23}$ +15° (*c*, 0·91), from methanol (Found: C, 75·6; H, 10·1. $C_{34}H_{54}O_5$ requires C, 75·2; H, 10·0%). The 2 : 4-*dinitrophenylhydrazone* of this keto-ester separated from alcohol in bright red needles, m. p. 240—243° (decomp.) (Found: N, 8·1. $C_{40}H_{58}O_8N_4$ requires N, 7·8%).

Deacetylation of 3-acetoxy-7-ketoeburic-8-enoic acid with boiling 10% alcoholic potassium hydroxide gave *3-hydroxy-7-ketoeburic-8-enoic acid* (XII; R = R′ = H) which crystallised from aqueous alcohol in feathery needles, m. p. 273—274°, $[\alpha]_D^{21}$ +14° (*c*, 1·76), $\lambda_{max.}$ 251 mμ (log ε 3·93) with an inflexion at about 315 mμ (log ε 2·16) (Found, in a specimen sublimed in a high vacuum: C, 76·2; H, 10·2. $C_{31}H_{50}O_4$ requires C, 76·5; H, 10·4%).

Methyl 3-Acetoxyeburic-7-enoate (XIII).—(*a*) A mixture of 3-hydroxy-7-ketoeburic-8-enoic acid (0·5 g.), 90% hydrazine hydrate (0·5 ml.), and diethylene glycol (10 ml.) was boiled for ½ hr., treated with sodium (0·5 g.) and diethylene glycol (5 ml.), then boiled for 5 hr., cooled, and poured into 3N-hydrochloric acid (30 ml.). Next day the solid was isolated with ether and successively esterified with ethereal diazomethane and acetylated with acetic anhydride–pyridine. A solution of the resulting product in light petroleum (30 ml.) was poured on a column of aluminium oxide (20 × 2 cm.) which was washed with light petroleum (500 ml.)

followed by benzene–light petroleum [3 portions each of mixtures (300 ml.) 1 : 99; 1 : 9; and 2 : 3]. *Methyl 3-acetoxyeburic-7-enoate* was then eluted from the column with benzene (500 ml.) and on purification from methanol obtained in long needles (0·26 g.), m. p. 172—174°, $[\alpha]_D^{20}$ +30° (*c*, 3·12; 0·5-dm. micro-tube) (Found: C, 77·0; H, 10·4. $C_{34}H_{56}O_4$ requires C, 77·2; H, 10·7%).

(*b*) A solution of methyl 3-acetoxyeburic-8-enoate (methyl *O*-acetyldihydroeburicoate, Part XVI) (2 g.) in acetic acid (100 ml.) at 10° was saturated with hydrogen chloride and poured on ice-water (300 ml.). After crystallisation from methanol the product, long needles (1·79 g.), m. p. 164—168°, was dissolved in light petroleum (75 ml.) and adsorbed on a column of aluminium oxide (24 × 2 cm.). On being washed with successive portions of solvent the chromatogram gave the following fractions which were crystallised from methanol: (1) with 300 ml. of light petroleum unchanged methyl 3-acetoxyeburic-8-enoate (0·29 g.), m. p. 157°; (2) 100 ml. of light petroleum, solid (0·17 g.), m. p. 163°; (3) 50 ml., solid (0·06 g.), m. p. 165°; (4)—(11) 1500 ml. of light petroleum, solid (0·5 g.), m. p. 167°; (12) 100 ml. of acetone–light petroleum (1 : 99), solid (0·02 g.), m. p. 167°; (13) 100 ml. of acetone–light petroleum (1 : 19), solid (0·71 g.), m. p. 166—168°; (14) 100 ml. of same mixture, oil (0·02 g.). The fractions (4)—(13) were combined and repeatedly crystallised from methanol, giving methyl 3-acetoxyeburic-7-enoate in long, colourless needles (1·02 g.) which gave a yellow colour with tetranitromethane in chloroform and had m. p. and mixed m. p. 172—174°, $[\alpha]_D^{20}$ +34° (*c*, 1·60) (Found: C, 77·3; H, 10·6%).

This compound could not be hydrogenated in acetic acid with hydrogen at atmospheric pressure and a platinum catalyst and, after treatment with hydrogen chloride in acetic acid, was recovered unchanged.

Oxidation of Methyl 3-Acetoxyeburic-7-enoate (XIII).—(*a*) A solution of this ester (0·5 g.), chromic anhydride (0·4 g.), acetic acid (15 ml.), and water (1 ml.) was kept at 80° for 1 hr., treated with a little methanol to destroy unchanged anhydride, and diluted with water (200 ml.). A solution of the yellow solid in benzene–light petroleum (1 : 1) (20 ml.) was poured on aluminium oxide (12 × 1·8 cm.). Eluted with acetone–benzene (1 : 19) (250 ml.), the resulting methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (XIV) separated from light petroleum or methanol in squat yellow prisms (0·39 g.), m. p. 171—172°, $[\alpha]_D^{20}$ +75° (*c*, 2·39; 0·5-dm. micro-tube), $\lambda_{max.}$ 270 mμ (log ε 3·92), identical with an authentic specimen.

(*b*) A mixture of methyl 3-acetoxyeburic-7-enoate (1 g.), selenium dioxide (1·5 g.), acetic acid (20 ml.), and water (0·25 ml.) was heated under reflux for 3 hr., cooled, filtered, and diluted with water (100 ml.). A solution of the solid in light petroleum (50 ml.) was poured on aluminium oxide (60 × 2 cm.), and the column then eluted with much light petroleum, giving methyl 3-acetoxyeburico-7 : 9(11)-dienoate (methyl *O*-acetyldehydrodihydroeburicoate, Part XVII) (XV) which crystallised from methanol in long, colourless needles (0·68 g.), m. p. 165—166°, $[\alpha]_D^{20}$ +66° (*c*, 1·77), $\lambda_{max.}$ 234, 243, 252 mμ (log ε 4·22, 4·28, and 4·11 respectively), identical with an authentic specimen.

Oxidation of Methyl 3-Acetoxy-7 : 11-diketoeburic-8-enoate (XIV) *with Selenium Dioxide.*—(*a*) A mixture of this ester (0·5 g.), selenium dioxide (1 g.), and nitrobenzene (5 ml.) was heated under reflux for 2 hr. and filtered, and the selenium and selenium dioxide were washed with ether. The combined filtrate and washings were extracted with 2N-sodium hydroxide (50 ml. × 5), then with 2N-hydrochloric acid, and finally with water. After the removal of the ether and nitrobenzene with steam the residual brown gum was dissolved in benzene–light petroleum (1 : 4) and the solution poured on aluminium oxide (16 × 1·3 cm.). Elution of the column in turn with benzene–light petroleum (1 : 4; 700 ml., and 800 ml.), and acetone–benzene (1 : 10; 500 ml.) gave three fractions which were combined and crystallised from alcohol, giving *methyl 3-acetoxy-7 : 11 : 12-triketoeburico-5 : 8-dienoate* (XVII) in orange-yellow needles (0·22 g.), m. p. 165—166°, $[\alpha]_D^{20}$ −79° (*c*, 0·45), $\lambda_{max.}$ 216, 286 mμ (log ε 4·04, 4·02) (Found: C, 71·6; H, 8·6. $C_{34}H_{48}O_7$ requires C, 71·8; H, 8·5%).

When this oxidation was repeated with more methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (4·5 g.) the fraction (2·97 g.) eluted from the column with benzene–light petroleum (1 : 4) and subsequently with benzene was the expected triketonic ester but a later fraction eluted with acetone–benzene (1 : 10) consisted of a compound believed to be *methyl 3-acetoxy-6 : 7 : 11 : 12-tetraketoeburic-8-enoate* which separated from aqueous alcohol in orange needles (0·12 g.), m. p. 194·5—195·5°, $[\alpha]_D^{23}$ −45° (*c*, 1·03), $\lambda_{max.}$ 294, 412—414 mμ (log ε 3·80, 2·51) (Found: C, 69·5; H, 8·7. $C_{34}H_{48}O_8$ requires C, 69·8; H, 8·3%). In a subsequent experiment with 21 g. of starting material this compound was not obtained; the only crystalline product was the triketonic ester (yield, 35%).

(*b*) A solution of methyl 3-acetoxy-7 : 11-diketoeburic-8-enoate (0·5 g.) in acetic anhydride (5 ml.), containing selenium dioxide (0·5 g.) was boiled for 3 hr., filtered (the solid washed with acetic acid), and poured into water. An ethereal solution of the resulting yellow product was extracted successively with 2N-sodium hydroxide (30 ml. × 5), 2N-hydrochloric acid, and water, dried, and evaporated. By chromatography from benzene–light petroleum (1 : 1; 50 ml.) on aluminium oxide (25 × 1·3 cm.) the residue was resolved into 2 fractions. Eluted with benzene–light petroleum (1 : 1, 50 ml.), fraction (1), a yellow gum mixed with needles (0·29 g.), consisted of *methyl* 3-*acetoxy*-7 : 11-*diketoeburico*-5 : 8-*dienoate* (XVI) which separated from methanol and then aqueous methanol in yellow needles (0·22 g.), m. p. 144—145°, $[\alpha]_D^{21}$ −1° (*c*, 1·12), $\lambda_{max.}$ 274 mμ (log ε 4·00), with an inflexion at about 370 mμ (log ε 2·18) (Found, in specimen sublimed in a high vacuum: C, 73·7; H, 8·9. $C_{34}H_{50}O_6$ requires C, 73·6; H, 9·1%).

Obtained by washing the column with more benzene–light petroleum (1 : 1; 200 ml.), fraction (2) was an orange gum (0·05 g.) which, on crystallisation from light petroleum and then alcohol, gave methyl 3-acetoxy-7 : 11 : 12-triketoeburico-5 : 8-dienoate in orange-yellow needles, m. p. 164—165°, identical with a specimen prepared by method (*a*).

Oxidation of methyl 3-acetoxy-7 : 11-diketoeburico-5 : 8-dienoate (0·08 g.) with selenium dioxide (0·08 g.) in boiling nitrobenzene (2 ml.) for 2 hr. gave a product from which only methyl 3-acetoxy-7 : 11 : 12-triketoeburico-5 : 8-dienoate was isolated by chromatography on aluminium oxide. Crystallised from alcohol, this formed orange-yellow needles (0·05 g.), m. p. 165—166°, $\lambda_{max.}$ 216, 286 mμ (log ε 4·05, 3·99), identical with an authentic specimen.

Reduction of Methyl 3-*Acetoxy*-7 : 11-*diketoeburic*-8-*enoate* (XIV).—On the addition of aluminium *iso*propoxide (30 g.) in *iso*propanol (75 ml.) the yellow solution of this ester (5 g.) in dioxan (50 ml.) became reddish-orange and was then heated on the steam-bath for 25 hr. with slow distillation of the solvent which was replaced by additions of *iso*propanol. Acetone (2 : 4-dinitrophenylhydrazone) was detected in the distillate during the first 8 hr.; the reaction was also followed by determinations of the ultra-violet spectrum of samples withdrawn at intervals, changing from $\lambda_{max.}$ 256—257 mμ after 9 hr. to $\lambda_{max.}$ 254 mμ ($E_{1\,cm.}^{1\%}$ cm. 141) after 17 hr. and $\lambda_{max.}$ 254 mμ ($E_{1\,cm.}^{1\%}$ cm. 143) after 25 hr. The mixture was then treated with an excess of 2N-hydrochloric acid, and the solid chromatographed on aluminium oxide from benzene (100 ml.). The combined fractions eluted with benzene (100 and 450 ml.), then acetone–benzene (1 : 10, 250 ml.; and 1 : 3, 100 ml.) which consisted of colourless gums (4·42 g.), $\lambda_{max.}$ 254—255 mμ, were dissolved in alcohol, and the solution was poured into water, giving a colourless granular precipitate, m. p. 185—190°, which did not crystallise. This was acetylated by the pyridine method and on crystallisation from alcohol and then light petroleum the product gave *methyl* 3 : 7-*diacetoxy*-11-*ketoeburic*-8-*enoate* (XVIII) in colourless needles (3·3 g.), m. p. 147—148°, $[\alpha]_D^{20}$ +102° (*c*, 1·05) (Found: C, 71·9; H, 9·4. $C_{36}H_{56}O_7$ requires C, 72·0; H, 9·4%). Under the usual conditions this compound did not react with 2 : 4-dinitrophenylhydrazine.

3-*Acetoxyeburic*-8-*enal*.—A mixture of 3-acetoxyeburic-8-enoic acid (*O*-acetyldihydroeburicoic acid, Part XVI) (5 g.), thionyl chloride (10 g.), and benzene (100 ml.) was heated under reflux for 3 hr. and evaporated, leaving 3-*acetoxyeburic*-8-*enoyl chloride* which separated from absolute acetone in colourless needles (3·5 g.), m. p. 175—177° (Found: C, 74·2; H, 9·7; Cl, 7·1. $C_{33}H_{53}O_3Cl$ requires C, 74·3; H, 10·0; Cl, 6·7%).

Hydrogen was led into a boiling solution of this chloride (2 g.) in *o*-xylene (200 ml.), containing 5% palladium–barium sulphate (2 g.), during 5 hr.; determination of the hydrogen chloride evolved with standard aqueous sodium hydroxide indicated that the reaction was complete. The mixture was evaporated in nitrogen under diminished pressure, the residue (1·8 g.) dissolved in light petroleum (100 ml.), and the solution poured on aluminium oxide (24 × 2 cm.). Elution with light petroleum (1·2 l.) gave 3-*acetoxyeburic*-8-*enal* which separated from alcohol in colourless leaflets (0·8 g.), m. p. 152—153° (decomp.), containing solvent of crystallisation. Sublimed in a high vacuum, the compound had m. p. 152—153°, $[\alpha]_D^{20}$ +70° (*c*, 3·0) (Found: C, 79·4; H, 10·7. $C_{33}H_{54}O_3$ requires C, 79·5; H, 10·9%). The *semicarbazone* formed needles, m. p. 263—265°, from alcohol (Found: N, 7·4. $C_{34}H_{57}O_3N_3$ requires N, 7·6%).

Eburic-8-*en*-3-*ol*.—(*a*) A mixture of 3-acetoxyeburic-8-enal (0·75 g.), potassium hydroxide (0·7 g.), 90% hydrazine hydrate (0·5 ml.), and diethylene glycol (5 ml.) was heated under reflux for 1½ hr., the excess of hydrazine hydrate distilled off, and the residue kept at 195° for 4 hr., cooled, diluted with water, and acidified. A solution of the dried precipitate (0·59 g.) in light petroleum was poured on a column of aluminium oxide (18 × 2 cm.) from which only traces of solid were obtained by washing successively with light petroleum, benzene, and acetone–benzene (1 : 19). Elution with acetone–benzene (1 : 9) then gave a crystalline solid (0·45 g.) which on recrystallisation from benzene–methanol (1 : 19) gave eburic-8-en-3-ol in needles, m. p. 166—

167°, $[\alpha]_D^{20}$ +54° (*c*, 3·2) (Found : C, 84·2; H, 12·3. Calc. for $C_{31}H_{54}O$: C, 84·1; H, 12·3%). The acetate separated from alcohol in plates, m. p. 130—131°, $[\alpha]_D^{20}$ +56° (*c*, 2·0) (Found : C, 81·9; H, 11·8. Calc. for $C_{33}H_{56}O_2$: C, 81·8; H, 11·6%).

(*b*) A mixture of 3-acetoxyeburic-8-enal semicarbazone (1·0 g.) and alcoholic sodium ethoxide (from 1·8 g. of sodium and 40 ml. of alcohol) was heated to 185° for 10 hr., cooled, diluted with water, and acidified with sulphuric acid. Crystallised from alcohol the precipitate gave eburic-8-en-3-ol in needles (0·32 g.), m. p. and mixed m. p. 166—167°, $[\alpha]_D^{20}$ +57° (*c*, 2·7) (Found : C, 84·2; H, 12·5%).

Concentration of the alcohol liquors from eburic-8-en-3-ol gave a small amount of a second product (50 mg.) which on repeated purification from alcohol had m. p. 165—166°, $[\alpha]_D^{20}$ +38° (*c*, 1·6) (Found: C, 84·5; H, 12·4%), and on admixture with eburic-8-en-3-ol had m. p. 155—157°.

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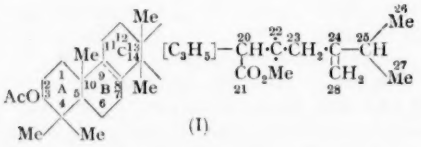
492. *The Chemistry of Fungi. Part XIX.* The Structure of Eburicoic Acid.*

By J. S. E. HOLKER, A. D. G. POWELL, ALEXANDER ROBERTSON, J. J. H. SIMES, R. S. WRIGHT, and (in part) R. M. GASCOIGNE.

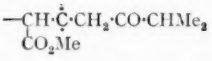
On treatment with acetic anhydride the hydrochloride of methyl *O*-acetyleburicoate gave a mixture of the dienes, methyl 3-acetoxyeburico-7 : 24(28)-dien-21-oate (IV) and methyl 3-acetoxyeburico-7 : 23-dien-21-oate (V). Ozonolysis of (V) furnished methyl *iso*propyl ketone and an amorphous aldehyde (VIII) which was characterised by oxidation to the αβ-unsaturated keto-ester (XII) and diketo-ester (XI). On oxidation with selenium dioxide *O*-acetyleburicoic acid gave a lactone shown to be 3-acetoxy-23-hydroxy-eburico-8 : 24(28)-dien-21-oic lactone (XIII; R = Ac).

The carboxyl group in eburicoic acid has been shown to be secondary and it is concluded that the side chain contains the residue –CH(CO_2H)·$\dot{C}$·CH_2·C(:CH_2)·$CHMe_2$. The transformation of eburicoic acid into lanost-8-ene confirms this and leads to a complete structure for eburicoic acid and its derivatives.

In Parts XVI (*J.*, 1951, 2346), XVII (*J.*, 1953, 1830) and XVIII * evidence was advanced that eburicoic acid is a tetracyclic dienoic acid of type (I) containing the rings A, B, and C of the lanosterol cyclic system together with a vinylidene group. The experimental work now described shows that the acid contains the side chain ·CH(CO_2H)·$\dot{C}$·CH_2·C(:CH_2)·$CHMe_2$. In this connection the steroid system of numbering the rings A, B, and C (Part XVIII) is now extended to cover this residue as in (I).



(I)



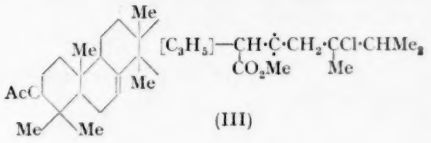
(II)

The infra-red absorption spectra of eburicoic acid and certain of its derivatives support the view that the reactive ethylenic double bond is present as a vinylidene group (cf. Part XVI). Thus the spectrum of eburicoic acid has a peak at 890 cm.$^{-1}$ characteristic of this group (Arnold, Koller, and Jeger, *Helv. Chim. Acta*, 1951, **34**, 555) whilst that of the ozonolysis product from methyl *O*-acetyleburicoate, which is now regarded as methyl 3-acetoxy-24-keto-28-noreburic-8-en-21-oate, shows peaks at 1730 cm.$^{-1}$, due to the acetoxy- and the carbomethoxy-group, and at 1715 cm.$^{-1}$ to the carbonyl group introduced by ozonolysis. Similarly, methyl 24-keto-28-noreburic-8-en-21-oate shows the same peaks. The observed infra-red frequency of the carbonyl absorption suggests that this group is

* Part XVIII, preceding paper.

exocyclic as in (II) or, less probably, in a six-membered ring system (cf. Grove and Willis, *J.*, 1951, 877). The possibility that the ozonolysis product, methyl 24-keto-28-noreburic-8-en-21-oate, was a methyl ketone was excluded by its failure to react with potassium hypoiodite at 80°.

On treatment with hydrogen chloride in acetic acid methyl *O*-acetyleburicoate gave an adduct in which the chlorine atom is labile. As expected, by analogy with methyl 3-acetoxyeburic-8-en-21-oate (methyl *O*-acetyldihydroeburicoate, Part XVII) this addition was accompanied by migration of the inert double bond from the Δ^8- to the Δ^7-position, thus giving (III). By the action of acetic anhydride on (III) hydrogen chloride was eliminated with the formation of two isomeric compounds which differ only in the position of the reactive double bond, *i.e.*, methyl 3-acetoxyeburico-7 : 24(28)-dien-21-oate (IV) and -7 : 23-dien-21-oate (V). Thus (IV) exhibited strong infra-red absorption at 823 and 890 cm.$^{-1}$, in the region of olefinic C–H out-of-plane bending where the former frequency is due to the trisubstituted nuclear double bond (cf. Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402) and the latter to the vinylidene group (cf. Arnold *et al.*, *loc. cit.*). On the other hand (V) had only one absorption peak at 823 cm.$^{-1}$, in this region of the spectrum and, since there are two double bonds present, clearly either both must be trisubstituted or one tri- and the other tetra-substituted. The relation between (IV) and (V) was ultimately confirmed by their hydrogenation to the same dihydro-derivative (VI), identical with methyl 3-acetoxyeburic-7-en-21-oate (3-acetoxyeburic-7-enate in Part XVIII). Further, oxidation of (VI) obtained from either source gave the same diketone (IX), identical with methyl 3-acetoxy-7 : 11-diketoeburic-8-en-21-oate (3-acetoxy-7 : 11-diketo-eburic-8-enate of Part XVII).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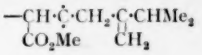
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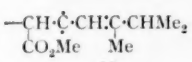
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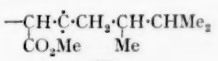
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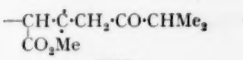
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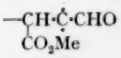
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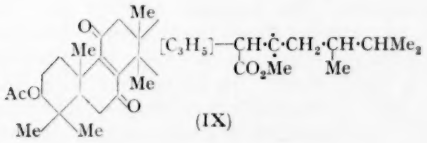
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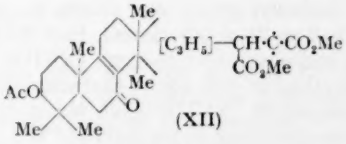
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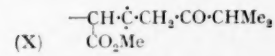
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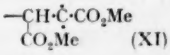
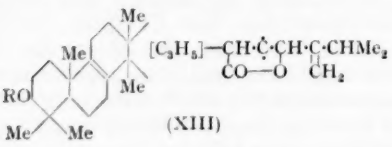

(XI)

That (IV) containing a methylene group differed from (I) only with regard to the position of the inactive (nuclear) double bond was established by the ozonolysis of (IV) to formaldehyde and methyl 3-acetoxy-24-keto-28-noreburic-7-en-21-oate (VII) which on oxidation with chromic anhydride furnished methyl 3-acetoxy-7 : 11 : 24-triketo-28-noreburic-8-en-21-oate (X), identical with the oxidation product obtained from methyl 3-acetoxy-24-keto-28-noreburic-8-en-21-oate (II). On the other hand, the ozonolysis of (V) gave methyl *iso*propyl ketone and an amorphous aldehydic product (VIII) which on oxidation with chromic anhydride under comparatively mild conditions and subsequent esterification furnished the αβ-unsaturated keto-ester (XII) whereas on more vigorous oxidation, followed by esterification of the product, (VIII) gave the yellow αβ-unsaturated diketo-ester (XI). Thus the side chain of eburicoic acid contains the residue $Me_2CH{\cdot}C(:CH_2){\cdot}CH_2{-}$.

By the oxidation of *O*-acetyleburicoic acid with an equivalent of selenium dioxide a

neutral product was obtained which is regarded as the lactone (XIII; R = Ac). The presence of the lactone ring was established by conversion into the acid (XVI) and this, on being heated, gave the lactone (XIII; R = H) which, on acetylation, regenerated the parent compound (XIII; R = Ac). In agreement with this the lactone (XIII; R = Ac) exhibited strong infra-red absorption at 890, 1730, and 1779 cm.$^{-1}$ characteristic



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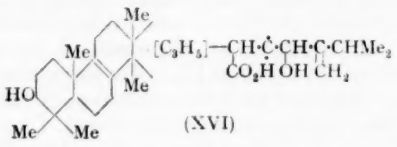
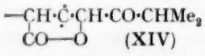
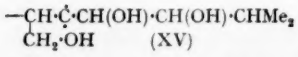


(XVI)

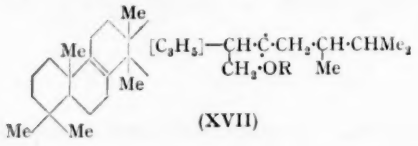


(XIV)

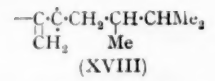


(XV)

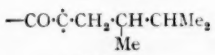
respectively of a vinyl, an acetoxy-, and a lactone group where the lactone is probably of the γ-type (cf. Grove and Willis, *loc. cit.*). Further, on ozonolysis (XIII; R = Ac) gave formaldehyde and 3-acetoxy-23-hydroxy-24-keto-28-noreburic-8-en-21-oic lactone (XIV; R = Ac) which, on reduction with lithium aluminium hydride, furnished 28-noreburic-8-ene-3 : 21 : 23 : 24-tetraol (XV; R = H). With lead tetra-acetate this tetraol yielded *iso*butyraldehyde which must arise by scission between $C_{(23)}$ and $C_{(24)}$, thus showing that hydroxylation of *O*-acetyleburicoic acid with selenium dioxide had taken place at $C_{(23)}$. Hence, on the view that the lactone ring present in (XIII; R = Ac) is five-membered, the carboxyl group in eburicoic acid is attached at $C_{(20)}$, *i.e.*, the side chain contains the residue $>C(CO_2H)\cdot\dot{C}\cdot CH_2\cdot C(:CH_2)\cdot CHMe_2$.



(XVII)



(XVIII)



(XIX)

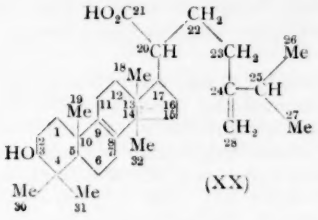
By the method which Arnold *et al.* (*loc. cit.*) employed in the case of elemadienolic acid this carboxyl group was shown to be secondary. The benzoate (XVII; R = Bz) of eburic-8-en-21-ol (eburicenol, Part XVI, *loc. cit.*) was pyrolysed in nitrogen, giving benzoic acid and eburico-8 : 20-diene (XVIII), the infra-red spectrum of which exhibited strong absorption at 887 cm.$^{-1}$ characteristic of a vinyl group. In agreement with this the ozonolysis of (XVIII) gave formaldehyde and 21-noreburic-8-en-20-one (XIX) having strong absorption in the infra-red at 1715 cm.$^{-1}$ characteristic of a non-conjugated exocyclic keto-group (cf. Grove and Willis, *loc. cit.*). Consequently, the foregoing expression for the side chain of eburicoic acid may be expanded to $\cdot CH(CO_2H)\cdot\dot{C}\cdot CH_2\cdot C(:CH_2)\cdot CHMe_2$.

In view of the tetracyclic nature of eburicoic acid and its established relation to lanosterol with respect to rings A, B, and C, in conjunction with the partial structure now established for the side chain, it appeared that the C_3H_5 residue is present in a *cyclo*pentane system as in lanosterol. Consequently, $C_{(22)}$ is present as a methylene group and, on the assumption that the side-chain is attached at $C_{(17)}$, the only difference between the carbon skeletons of eburicoic acid and lanosterol appeared to be the presence of the extra carbon atom $C_{(28)}$ in the side chain of the acid. Therefore, from the established structure of lanosterol (Curtis, Fridrichsons, and Mathieson, *Nature*, 1952, **170**, 321; Voser, Mijovic, Heusser, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1952, **35**, 2414; Barnes, Barton, Fawcett, and Thomas, *J.*, 1953, 576) eburicoic acid may be represented by (XX). Since the position of the methylene group in the side chain of eburicoic acid has been established, the following conversion of methyl 24-keto-28-noreburic-8-en-21-oate (XXI) into lanost-8-ene (lanostene; Ruzicka, Rey, and Muhr; *Helv. Chim. Acta*, 1944, **27**, 472; Ruzicka, Denss, and Jeger, *ibid.*, 1945, **28**, 759; Dorée, McGhie, and Kurzer, *J.*, 1947, 1467) provides

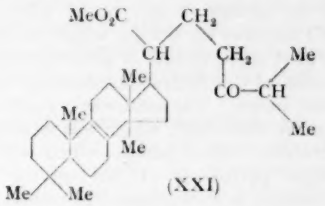
conclusive evidence in support of this structure (XX) for eburicoic acid and further, in the absence of steric rearrangements during its conversion into (XXII; R = Me), eburicoic acid has the same configuration as lanosterol.

On reduction by the Wolff–Kishner method followed by esterification of the product, methyl 24-keto-28-noreburic-8-en-21-oate gave methyl 28-noreburic-8-en-21-oate (XXII; R = CO_2Me) which was reduced with lithium aluminium hydride to 28-noreburic-8-en-21-ol (XXII; R = CH_2·OH). Oxidised by the Oppenauer procedure, this alcohol furnished 28-noreburic-8-en-21-al (XXII; R = CHO), and by the Wolff–Kishner method this aldehyde gave 28-noreburic-8-ene (XXII; R = Me) which, by comparison of their melting points, specific rotations, and infra-red absorption spectra, was found to be identical with lanost-8-ene. It is of interest that, in respect of the carbon skeletons of their side chains, lanosterol bears the same relation to eburicoic acid as cholesterol to ergosterol.

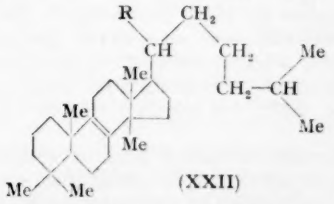
With regard to the stereochemical relation of eburicoic acid and lanosterol, there is evidence that the configurations of the hydroxyl groups at $C_{(3)}$ are identical, *viz.*, the reduction of 3-ketoeburico-8 : 24(28)-dien-21-oic acid with sodium and alcohol gives eburicoic acid without the respective epimer (Part XVII), and dehydration of methyl 3-hydroxyeburic-8-en-21-oate with phosphorus pentachloride is accompanied by rearrangement of ring A (Part XVI) (cf. Barnes *et al.*, *loc. cit.*).



(XX)



(XXI)



(XXII)

In the formation of methyl eburic-8-en-21-oate from eburicoic acid by the use of Oppenauer and Wolff–Kishner procedures (Part XVI) stereochemical rearrangement appeared not to occur because the same product was obtained on hydrogenation of methyl eburico-2 : 8-dien-21-oate formed by the dehydration of methyl 3-hydroxyeburic-8-en-21-oate with phosphoryl chloride (Part XVIII) (cf. the conversion of lanosterol into lanost-8-ene; Dorée *et al.*, *loc. cit.*; McGhie, Pradhan, and Cavalla, *J.*, 1952, 3176). Since in the formation of methyl 28-noreburic-8-en-21-oate (XXII; R = CO_2Me) from eburicoic acid the same methods are employed it seems unlikely that this transformation was accompanied by steric rearrangement. For the conversion of methyl 28-noreburic-8-en-21-oate (XXII; R = CO_2Me) into lanost-8-ene the same procedures have been employed and it seems unlikely, therefore, that stereochemical rearrangement of the cyclic system occurs. The possibility of inversion at $C_{(20)}$ during transformation of (XXII; R = CO_2Me) into (XXII; R = Me) cannot at present be excluded although this is regarded as unlikely.

The steroid numbering of the molecule is now extended to include ring D and the angular methyl groups attached at $C_{(10)}$ and $C_{(13)}$. In accordance with the Editorial Report on Nomenclature, Appendix C, Steroid Nomenclature, Rule 1 (*J.*, 1951, 3526), the number 29, which is reserved for a carbon atom attached at $C_{(28)}$, is omitted and the angular methyl groups attached at $C_{(4)}$ and $C_{(14)}$ are numbered 30, 31, and 32 respectively as in (XX), a system which was adopted after discussion with Professor E. R. H. Jones, F.R.S., and Dr. T. G. Halsall of the University of Manchester.

Experimental

Unless stated otherwise light petroleum employed had b. p. 60—80°, optical rotations were measured in chloroform at room temperature (18—22°), ultra-violet absorption spectra in 95% alcohol, and infra-red spectra in 20% carbon disulphide solutions.

Methyl 24-Keto-28-noreburic-8-en-21-oate (XXI).—A current of ozone and oxygen was led into a solution of methyl eburico-8 : 24(28)-dien-21-oate (methyleburicodienate, Part XVI, *loc. cit.*) (2·5 g.) in acetic acid (250 ml.) for 2·5 hr. After the dilution of the mixture with water (2 l.) the formaldehyde was distilled with steam and converted into the dimedone derivative (0·92 g., 56%). The non-volatile residue was collected and chromatographed on aluminium oxide (24 × 1·6 cm.) from light petroleum (50 ml.). After being washed with light petroleum (400 ml.) to remove amorphous material (0·56 g.), the column was extracted with more light petroleum (200 ml.) and then benzene–light petroleum (1 : 1; 800 ml.), giving *methyl 24-keto-28-noreburic-8-en-21-oate* which separated from methanol in needles (1·5 g.), m. p. 123—125°, $[\alpha]_D$ +50° (*c*, 3·0; *l* = 0·5 dm.) (Found : C, 79·4; H, 10·7. $C_{31}H_{50}O_3$ requires C, 79·1; H, 10·7%). The *oxime* formed prisms, m. p. 158—160° (decomp.), from alcohol (Found : N, 2·9. $C_{31}H_{51}O_3N$ requires N, 2·9%).

Action of Hydrogen Chloride on Methyl O-Acetyleburicoate.—A solution of this ester (10 g.) in acetic acid (600 ml.) kept at room temperature was slowly saturated with hydrogen chloride and then poured into ice-water (1 l.). On isolation the resulting *hydrochloride* (III) separated from methanol in needles (8 g.), m. p. 173° (decomp.), $[\alpha]_D$ +33° (*c*, 1·97) (Found : Cl, 6·2. $C_{34}H_{55}O_4Cl$ requires Cl, 6·3%), which on treatment with dilute alcoholic silver nitrate instantaneously gave a precipitate of silver chloride.

A solution of this hydrochloride (2 g.) in acetic anhydride (25 ml.) was boiled for 10 hr. and diluted with water. The solid was crystallised twice from methanol, giving a fraction in needles (1·03 g.), m. p. 165—168°, which was adsorbed on aluminium oxide (100 g.; 24 × 2·2 cm.) from light petroleum. After being washed with the same solvent the column was extracted with acetone–light petroleum (1 : 99), giving *methyl 3-acetoxyeburico-7 : 24(28)-dien-21-oate* (IV) which separated from methanol in needles, m. p. 173—174°, $[\alpha]_D$ +32° (*c*, 2·66) (Found : C, 77·4; H, 10·1. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·3%). The methanolic liquors left on separation of the solid, m. p. 165—168°, were concentrated, giving a solid (0·74 g.), m. p. 125—135°. From this material *methyl 3-acetoxyeburico-7 : 23-dien-21-oate* (V) was isolated by the same chromatographic technique and, on crystallisation from methanol, formed fine needles, m. p. 153—154°, $[\alpha]_D$ +32° (*c*, 2·47; *l* = 0·5 dm.) (Found : C, 77·9; H, 10·4. $C_{34}H_{54}O_4$ requires C, 77·5; H, 10·3%).

Hydrogenation (1 mol. absorbed) of methyl 3-acetoxyeburico-7 : 24(28)-dien-21-oate (IV) in acetic acid, with a platinum catalyst, gave an almost theoretical yield of methyl 3-acetoxyeburic-7-en-21-oate (VI) which was purified by chromatography and then from alcohol, forming needles, m. p. 172—174°, identical with an authentic specimen (Part XVIII). This hydrogenation product (1 g.) was oxidised with chromic anhydride (0·8 g.) in 95% acetic acid (30 ml.) at 80° during 1 hr., the excess of chromic acid was destroyed with a little methanol, and the product was precipitated with water (350 ml.). A solution of this in benzene–light petroleum (1 : 1; 30 ml.) was poured on aluminium oxide (17 × 1·8 cm.) which was then washed with acetone–benzene (1 : 19; 100 ml.), giving methyl 3-acetoxy-7 : 11-diketoeburic-8-en-21-oate (IX) which separated from methanol in large yellow prisms (0·41 g.), m. p. 171—172°, $[\alpha]_D$ +68° (*c*, 2·07; *l* = 0·5 dm.), $\lambda_{max.}$ 270 mμ (log ε 3·92), identical with an authentic specimen (methyl *O*-acetyldihydrodiketoeburicoate, Part XVII).

Ozonolysis of methyl 3-acetoxyeburico-7 : 24(28)-dien-21-oate (1 g.) in acetic acid (100 ml.), and decomposition of the product with water (1 l.) gave formaldehyde, isolated as the dimedone derivative (0·33 g.), m. p. 189°, and *methyl 3-acetoxy-24-keto-28-noreburic-7-en-21-oate* (VII), which formed needles (0·78 g.), m. p. 169—170°, $[\alpha]_D$ +45° (*c*, 1·08), from methanol (Found : C, 75·1; H, 9·6. $C_{33}H_{52}O_5$ requires C, 74·9; H, 9·9%). On oxidation by chromic anhydride–acetic acid this compound furnished methyl 3-acetoxy-7 : 11 : 24-triketo-28-noreburic-8-en-21-oate (X) which separated from light petroleum in yellow needles, m. p. 194—195°, $[\alpha]_D$ +75° (*c*, 0·91; *l* = 0·5 dm.), $\lambda_{max.}$ 270 mμ (log ε 3·94) (Found : C, 71·5; H, 9·1. Calc. for $C_{33}H_{48}O_7$: C, 71·3; H, 8·7%). This product was also prepared from methyl 3-acetoxyeburico-8 : 24(28)-dien-21-oate (methyl *O*-acetyleburicoate) (I) by the same two-stage procedure and appeared to be identical with the ester which Lahey and Strasser (*J.*, 1951, 873) obtained by the vigorous oxidation of (I) with chromic anhydride.

Hydrogenation (1 mol. of hydrogen absorbed) of methyl 3-acetoxyeburico-7 : 23-dien-21-oate

(V) furnished methyl 3-acetoxyeburic-7-en-21-oate (VI) which had m. p. and mixed m. p. 172—174°, after purification by chromatography and crystallisation from methanol and on oxidation with chromic anhydride in acetic acid gave methyl 3-acetoxy-7 : 11-diketoeburic-8-en-21-oate (IX), m. p. and mixed m. p. 171—172°.

Ozonolysis of methyl 3-acetoxyeburico-7 : 23-dien-21-oate (1 g.) in acetic acid (100 ml.) and treatment of the solution with water (1 l.), followed by distillation in steam, gave a distillate which on treatment with 1% aqueous dimedone gave the formaldehyde derivative (0·08 g.), m. p. 189°. The filtrate from the solid was distilled and mixed with 1% aqueous 2 : 4-dinitrophenylhydrazine sulphate (50 ml.), giving the 2 : 4-dinitrophenylhydrazone (0·24 g.) of methyl *iso*propyl ketone which was purified by chromatography on aluminium oxide and then from alcohol, forming orange needles, m. p. 123—124°, $\lambda_{max.}$ 227, 361 mμ (log ε 4·30, 4·38), identical with an authentic specimen (Found : C, 49·8; H, 5·4; N, 21·2. Calc. for $C_{11}H_{14}O_4N_4$: C, 49·6; H, 5·3; N, 21·0%).

The non-volatile ozonolysis product (0·93 g.), which had aldehydic properties, did not crystallise. A solution of the crude substance (0·9 g.) in acetic acid (20 ml.) was mixed with chromic anhydride (0·22 g.) in acetic acid (6·6 ml.) and kept at 40° for 1 hr. Next day the product was precipitated with water (200 ml.) and isolated along with a little acetic acid by means of ether. After the removal of the acetic acid in a vacuum at room temperature the solid was dissolved in ether, and the solution extracted with 2N-sodium hydroxide. The alkaline extracts were acidified and the acidic material esterified with ethereal diazomethane. A solution of the resulting ester in benzene–light petroleum (1 : 4; 5 ml.) was poured on aluminium oxide (12 × 0·8 cm.), and the column washed with benzene–light petroleum (9 : 1), giving the *keto-ester* (XII) which separated from aqueous methanol in colourless needles, m. p. 196—198°, $[\alpha]_D$ +14° (*c*, 1·0; *l* = 0·5 dm.), $\lambda_{max.}$ 251 mμ (log ε 3·76) (Found : C, 69·8; H, 8·9. $C_{30}H_{44}O_7$ requires C, 69·7; H, 8·6%).

When the non-volatile solid (1·78 g.) was oxidised with chromic anhydride (1·95 g.) in 95% acetic acid (60 ml.) at 80° and the product isolated and esterified by the same procedure the αβ-unsaturated *diketo*-ester (XI) was obtained. This was purified by chromatography on aluminium oxide from benzene–light petroleum and then crystallised from chloroform–light petroleum, forming yellow plates, m. p. 209—212°, $[\alpha]_D$ +71° (*c*, 1·18; *l* = 0·5 dm.), $\lambda_{max.}$ 270 mμ (log ε 3·94) (Found : C, 67·8; H, 8·0. $C_{30}H_{42}O_8$ requires C, 67·9; H, 8·0%).

3-*Acetoxy*-23-*hydroxyeburico*-8 : 24(28)-*dien*-21-*oic Lactone*.—A solution of *O*-acetyleburicoic acid (9 g.) in acetic acid (135 ml.) containing selenium dioxide (1 g.) and water (4·5 ml.) was heated under reflux for 3 hr., filtered, and poured into water. The dried precipitate (8·9 g.), dissolved in benzene–light petroleum (1 : 4) (300 ml.), was poured on neutralised aluminium oxide (30 × 2·9 cm.; 200 g.), and the column extracted with benzene–light petroleum (1 : 4; 400 ml.), giving a white solid (4·5 g.) which, on crystallisation from alcohol, yielded 3-*acetoxy*-23-*hydroxyeburico*-8 : 24(28)-*dien*-21-*oic lactone* (XIII; R = Ac) in plates (2·6 g.), m. p. 214—215°, $[\alpha]_D$ +49° (*c*, 2·0) (Found : C, 77·3; H, 9·6. $C_{33}H_{50}O_4$ requires C, 77·6; H, 9·9%). A solution of this lactone (0·5 g.) in 10% alcoholic potassium hydroxide (20 ml.) was boiled for 1 hr., diluted with water (100 ml.), cooled to 0°, and acidified with acetic acid, giving 3 : 23-*dihydroxyeburico*-8 : 24(28)-*dien*-21-*oic acid* (XVI) which formed slender needles, m. p. 216° (decomp.), $[\alpha]_D$ +49° (*c*, 2·16 in EtOH; *l* = 0·5 dm.), from ethyl acetate (Found : C, 76·7; H, 10·2. $C_{31}H_{50}O_4$ requires C, 76·5; H, 10·4%). On being kept at 216° until effervescence had ceased this acid was quantitatively converted into 3 : 23-*dihydroxyeburico*-8 : 24(28)-*dien*-21-*oic lactone* (XIII; R = H) which separated from methanol in slender needles, m. p. 181—182°, $[\alpha]_D$ +48° (*c*, 1·62; *l* = 0·5 dm.) (Found : C, 79·5; H, 10·3. $C_{31}H_{48}O_3$ requires C, 79·4; H, 10·3%). On acetylation by acetic anhydride–pyridine this regenerated the acetate, m. p. and mixed m. p. 214—215°.

3-*Acetoxy*-23-*hydroxy*-24-*keto*-28-*noreburic*-8-*en*-21-*oic Lactone* (XIV; R = Ac).—Ozonolysis of 3-acetoxy-23-hydroxyeburico-8 : 24(28)-dien-21-oic lactone (8 g. in batches of 1 g.) in acetic acid gave formaldehyde, isolated as the dimedone derivative (yield, 44%), and 3-*acetoxy*-23-*hydroxy*-24-*keto*-28-*noreburic*-8-*en*-21-*oic lactone* (XIV; R = Ac) (7·4 g.) which was purified by filtration through aluminium oxide (32 × 1·8 cm.) from benzene–light petroleum (200 ml.) followed by crystallisation from benzene–alcohol (1 : 10), forming plates (4·9 g.), m. p. 233—235°, $[\alpha]_D$ +59° (*c*, 2·05) (Found : C, 75·2; H, 9·5. $C_{32}H_{48}O_5$ requires C, 74·9; H, 9·4%). The *oxime* separated from methanol in needles, m. p. 231° (decomp.) (Found : N, 2·7. $C_{32}H_{49}O_5N$ requires N, 2·7%).

Reduction of this lactone (1·5 g.) with lithium aluminium hydride (5 g.) in boiling ether for 10 hr., followed by treatment of the reaction mixture with ice and dilute sulphuric acid, gave

28-*noreburic*-8-*ene*-3 : 21 : 23 : 24-*tetrol* (XV; R = H) which was isolated with ether and crystallised from alcohol–ethyl acetate (1 : 20), forming slender needles (1·1 g.), m. p. 214—215·5°, $[\alpha]_D$ +53° (*c*, 2·0 in EtOH) (Found, in specimen sublimed in a high vacuum : C, 75·3; H, 10·8. $C_{30}H_{52}O_4$ requires C, 75·6; H, 11·0%). On acetylation by acetic anhydride–pyridine this gave the *tetra-acetate*, forming needles, m. p. 100°, $[\alpha]_D$ +53° (*c*, 2·37), from dilute alcohol (Found : C, 71·2; H, 9·1. $C_{38}H_{60}O_8$ requires C, 70·8; H, 9·4%).

Oxidation of this tetrol (0·4 g.) with lead tetra-acetate (0·37 g.) in acetic acid (9 ml.) at room temperature was complete after 4 hr. Dilution with water then gave an amorphous solid which reduced Fehling's solution, formed an amorphous 2 : 4-dinitrophenylhydrazone, and on oxidation with chromic anhydride in acetic acid yielded intractable material.

Distillation of the aqueous-acetic acid filtrate from the solid gave *iso*butyraldehyde which was isolated as the 2 : 4-dinitrophenylhydrazone, m. p. 181—182°, after purification from alcohol, identical with an authentic specimen (yield, 44%) (Found : N, 22·3. Calc. for $C_{10}H_{12}N_4O_4$: N, 22·2%).

21-*Noreburic*-8-*en*-20-*one* (XIX).—Eburic-8-en-21-ol (XVII; R = H) (eburicenol, Part XVI) (3·5 g.) was benzoylated in pyridine. The resulting *benzoate* (XVII; R = Bz) separated from methanol in needles (2·9 g.), m. p. 100—102°, $[\alpha]_D$ +40° (*c*, 2·0) (Found : C, 83·9; H, 10·7. $C_{38}H_{58}O_2$ requires C, 83·5; H, 10·7%). On being kept in nitrogen at 340—350° for 2 hr. this (2·7 g.) gave a sublimate of benzoic acid. A solution of the residue in a mixture of benzene (135 ml.) and 10% methanolic potassium hydroxide (225 ml.) was boiled for 1½ hr. to hydrolyse unchanged benzoate, and then poured into water. The mixture was extracted with ether, and the ethereal extracts were washed with 2N-sodium hydroxide, dried, and evaporated, leaving a colourless oil. A solution of this in light petroleum (50 ml.) was poured on aluminium oxide (24 × 1·6 cm.), and the column eluted with the same solvent. Evaporation of the eluate left *eburico*-8 : 20-*diene* (XVIII) which separated from acetone in plates (0·98 g.), m. p. 73—74°, $[\alpha]_D$ +45° (*c*, 2·01; *l* = 0·5 dm.) (Found : C, 87·6; H, 12·3. $C_{31}H_{52}$ requires C, 87·7; H, 12·3%). Subsequent elution of the aluminium oxide with acetone–benzene (1 : 20) gave eburic-8-en-21-ol (1·4 g.), m. p. and mixed m. p. 100—102°.

Ozonolysis of eburico-8 : 20-diene (0·42 g.) in acetic acid (100 ml.) gave formaldehyde, isolated as the dimedone derivative, m. p. 189° (yield, 31%), and 21-*noreburic*-8-*en*-20-*one* (XIX) which separated from methanol in needles (0·22 g.), m. p. 101—102°, $[\alpha]_D$ +98° (*c*, 2·98; *l* = 0·5 dm.) (Found : C, 84·8; H, 11·9. $C_{30}H_{50}O$ requires C, 84·5; H, 11·8%). The *oxime* separated from dilute alcohol in needles, m. p. 137° (Found : N, 3·2. $C_{30}H_{51}ON$ requires N, 3·2%).

Methyl 28-*Noreburic*-8-*en*-21-*oate* (XXII; R = CO_2Me).—A mixture of methyl 24-keto-28-noreburic-8-en-21-oate (XXI) (2·6 g.), 90% hydrazine hydrate (0·8 ml.), potassium hydroxide (1·2 g.), and diethylene glycol (8 ml.) was heated under reflux for 3 hr. and then at 195° for 5 hr. The cooled mixture was poured into 3N-hydrochloric acid (18 ml.), and the precipitate collected, washed, dried, and treated with ethereal diazomethane. A solution of the resulting product in light petroleum (50 ml.) was poured on a column of aluminium oxide (20 × 2 cm.), and this eluted successively with (*a*) light petroleum (120 ml.), (*b*) light petroleum (200 ml.), (*c*) benzene–light petroleum (1 : 10; 50 ml.) and (*d*) benzene–light petroleum (1 : 1; 50 ml.). Evaporation of the eluate (*a*) gave amorphous material, whilst (*b*), (*c*), and (*d*) yielded a crystalline product (1·28 g.) which on crystallisation from methanol gave *methyl* 28-*noreburic*-8-*en*-21-*oate* in needles, m. p. 107—108°, $[\alpha]_D$ +48° (*c*, 1·0) (Found : C, 81·9; H, 11·3. $C_{31}H_{52}O_2$ requires C, 81·6; H, 11·4%). Further elution of the column with acetone–benzene gave intractable products.

28-*Noreburic*-8-*en*-21-*ol* (XXII; R = CH_2·OH).—A solution of methyl 28-noreburic-8-en-21-oate (0·9 g.) in ether (150 ml.) containing lithium aluminium hydride (1 g.) was heated under reflux for 6 hr. Next day the excess of lithium aluminium hydride was destroyed with ethereal ethyl acetate, the mixture was poured into 2N-sulphuric acid, and the product was isolated with ether. Crystallised from methanol, this gave 28-*noreburic*-8-*en*-21-*ol* in needles (0·7 g.), m. p. 104—105·5°, $[\alpha]_D$ +58° (*c*, 1·6) (Found : C, 84·2; H, 12·1. $C_{30}H_{52}O$ requires C, 84·1; H, 12·1%).

28-*Noreburic*-8-*en*-21-*al* (XXII; R = CHO).—A mixture of 28-noreburic-8-en-21-ol (0·65 g.), benzoquinone (1·6 g.), aluminium *tert.*-butoxide (1·1 g.), and benzene (50 ml.) was heated under reflux for 14 hr. with the addition of more aluminium *tert.*-butoxide (0·5 g.) after 3 hr. This was poured into 2N-sulphuric acid (15 ml.), the excess of benzoquinone and *tert.*-butyl alcohol was removed with steam, the residue was extracted repeatedly with ether, and the combined extracts were washed with 0·5N-sodium hydroxide (50 ml. × 4) and then water (50 ml. × 4) and then dried. Crystallised from alcohol, the residue gave 28-noreburic-8-en-21-al (0·5 g.) in

plates, m. p. 126—128°, $[\alpha]_D$ +65° (*c*, 1·1; *l* = 0·5 dm.) (Found: C, 84·3; H, 11·5. $C_{30}H_{50}O$ requires C, 84·5; H, 11·7%).

Lanost-8-ene (28-*Noreburic-8-ene*) (XXII; R = Me).—The hydrazone of the aldehyde (XXII; R = CHO) (0·2 g.) was reduced by the method used for 24-keto-28-noreburic-8-en-21-oate, and the product (0·18 g.) was chromatographed on aluminium oxide (17 × 1·2 cm.) from light petroleum (20 ml.). Elution with light petroleum (75 ml.) gave 28-noreburic-8-ene, m. p. 73—74°, $[\alpha]_D$ +67° (*c*, 2·6; *l* = 0·5 dm.) (Found: C, 87·1; H, 12·7. Calc. for $C_{30}H_{52}$: C, 87·4; H, 12·6%). Thus obtained, 28-noreburic-8-ene was identical with a specimen of lanost-8-ene, m. p. 73—74°, $[\alpha]_D$ 66° (*c*, 1·08; *l* = 0·5 dm.), prepared by the method of McGhie *et al.* (*loc. cit.*) from lanost-8-en-3-one (lanostenone) which was derived from lanost-8-en-3-ol (dihydrolanosterol) by the following procedure (cf. Ruzicka, Denss, and Jeger, *loc. cit.*). A mixture of lanost-8-en-3-ol (2 g.), *cyclo*hexanone (5 ml.), aluminium *tert.*-butoxide (4 g.), and dioxan (30 ml.) was heated under reflux for 7 hr., cooled, and poured into 2N-sulphuric acid (30 ml.). After the removal of unchanged *cyclo*hexanone and dioxan with steam the product (1·5 g.) was isolated with ether and chromatographed from light petroleum (100 ml.) on aluminium oxide (15 × 2 cm.). The fractions obtained by eluting the column successively with benzene–light petroleum (1 : 10; 100 ml.), (1 : 5; 50 ml.), and (4 : 5; 50 ml.) were combined and crystallised from acetone–methanol, giving lanost-8-en-3-one in plates (0·9 g.), m. p. 119—120°, $[\alpha]_D$ +68° (*c*, 1·16) (Found: C, 84·9; H, 11·7. Calc. for $C_{30}H_{50}O$: C, 84·5; H, 11·7%).

Reduction of 3-*Ketoeburico*-8 : 24(28)-*dien*-21-*oic Acid*.—Sodium (8 g.) was added portionwise to a boiling solution of this acid (eburicodienonic acid, Part XVI) (0·35 g.) in alcohol (100 ml.) during 4 hr. with the addition of sufficient alcohol (in all 25 ml.) to maintain a clear solution. The mixture was poured into an excess of 2N-hydrochloric acid, the alcohol removed with steam, and the product collected, dried, and chromatographed from benzene (100 ml.) on neutralised aluminium oxide (26 × 1·5 cm.). The column was eluted with (*a*) benzene (800 ml.) and then acetone–benzene (*b*) (1 : 19; 250 ml.), (*c*) (1 : 9; 250 ml.), (*d*) (1 : 4; 1050 ml.), and (*e*) (1 : 1; 500 ml.). On evaporation fractions (*a*) and (*b*) gave a yellow gum (0·03 g.), and (*c*), (*d*), and (*e*) eburicoic acid (0·01 g.), (0·2 g.), and (0·05 g.) which on crystallisation had m. p. 287—289°, identical with an authentic specimen (Found: C, 78·9; H, 10·5. Calc. for $C_{31}H_{50}O_3$: C, 79·1; H, 10·7%). Prepared by pyridine–acetic anhydride, the acetyl derivative had m. p. and mixed m. p. 252—254° (Found: C, 77·0; H, 9·9. Calc. for $C_{33}H_{52}O_4$: C, 77·3; H, 10·2%).

The authors thank J. G. Reynolds and R. A. G. Carrington of the Spectroscopic Section, Thornton Research Centre, Shell Petroleum Co. Ltd., for the measurement of infra-red spectra on solid films of lanost-8-ene derived from eburicoic acid and lanosterol. One of them (R. S. W.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Grant.

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493. *The Chemistry of Fungi. Part XX.* Metabolites of* Chaetomium indicum *Corda.*

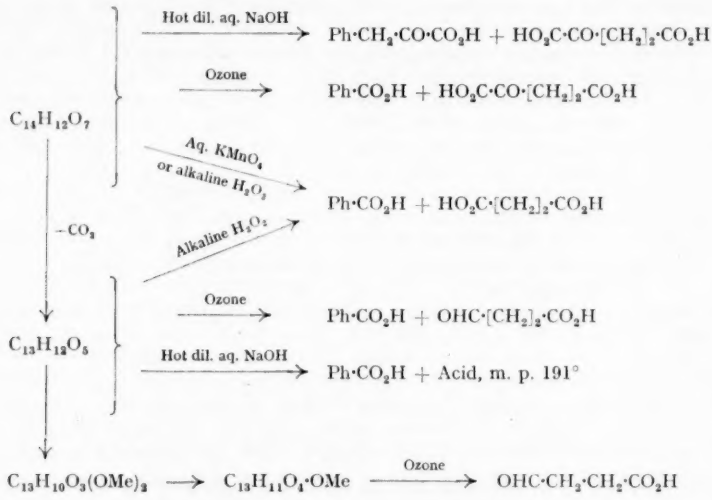
By D. H. JOHNSON, ALEXANDER ROBERTSON, and W. B. WHALLEY.

The isolation of a tribasic acid $C_{14}H_{12}O_7$ and two nitrogenous acids from the metabolic liquors of *Chaetomium indicum* Corda grown on Czapek–Dox medium is recorded. The acid $C_{14}H_{12}O_7$ is shown to be 4-carboxy-2-oxo-3-phenylhept-3-enedioic acid (I), or, less probably, the δ-lactone of type (III) derived from it.

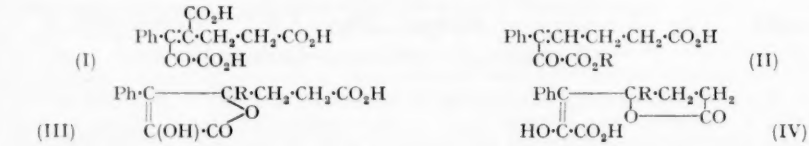
IN an examination of the metabolic products of the genus *Chaetomium* of the Ascomycetes Fungi the growth of *C. indicum* Corda on a Czapek–Dox medium gave a clear orange metabolic liquor from which an acid $C_{14}H_{12}O_7$ was isolated along with small amounts of two nitrogenous products (A) and (B). This acidic metabolite, which had an intense green ferric reaction, was optically inactive and on potentiometric titration behaved as a tribasic acid with, curiously, only one point of inflexion on the pH titration curve, indicating that the three acidic groups are of similar strength; on esterification with ethereal diazo-

* Part XIX, preceding paper.

methane it gave a trimethyl derivative. The metabolite did not react with the usual carbonyl reagents and behaved as a saturated compound towards perbenzoic acid, bromine in acetic acid or chloroform, and hydrogen in the presence of palladium–charcoal or Raney nickel. On being heated in a vacuum at 180° or boiled with dilute sulphuric acid the compound lost a molecule of carbon dioxide and yielded a dibasic acid $C_{13}H_{12}O_5$, which had the same green ferric reaction and was characterised by the formation of a dimethyl derivative. Like the parent compound this acid failed to react with carbonyl reagents, bromine, perbenzoic acid, or hydrogen in the presence of a catalyst. The annexed scheme summarises the reactions and degradations of the metabolite $C_{14}H_{12}O_7$ and its decarboxylation product $C_{13}H_{12}O_5$.



The production of the decomposition products indicated strongly supports the view that the acid $C_{14}H_{12}O_7$ is 4-carboxy-2-oxo-3-phenylhept-3-enedioic acid (I), and similarly its decarboxylation product is 2-oxo-3-phenylhept-3-enedioic acid (II; R = H). These formulations, however, do not account for the characteristic intense ferric reactions of the acids which, curiously, are not given by their methyl derivatives.



Clearly the acids formulated as (I) and (II; R = H) could give rise to lactones of two types (III and IV; R = CO_2H), and (III and IV; R = H) which would account for the ferric reactions exhibited by the metabolite and its decarboxylation product. Nevertheless, on the basis of the degradation experiments recorded, apart from the ferric reactions, we regard these acids as being represented by formula (I) and (II; R = H) respectively. In support of this it may be noted, *inter alia*, that on ozonolysis the metabolite gives α-oxoglutaric acid whilst the monomethyl ester of its decarboxylation product yields β-formylpropionic acid, which also serves to show that this ester has formula (II; R = Me). In an attempt to differentiate further between the structures of types (I) and (III) the infra-red absorption spectra of the metabolite and its decarboxylation product were kindly examined for us by Dr. A. J. Ham of the Shell Petroleum Company Ltd. Although there appears to be some evidence against the lactone formula, in the absence of data for

analogous compounds the results were inconclusive. With regard to the ferric reactions exhibited by these compounds it may well be that they are due to the presence of small amounts of the lactone forms.

Owing to lack of material the nature of the acid, m. p. 191°, formed in small amounts along with benzoic acid by treatment of the acid $C_{13}H_{12}O_5$ with alkali has not been defined. It does not react with carbonyl reagents and has a negative ferric reaction. By analogy with the formation of α-oxoglutaric acid from (I) the expected product would have been β-formylpropionic acid. This compound (Wislicenus, Boklen, and Reuthe, *Annalen*, 1908, **363**, 353; Perkin and Sprankling, *J.*, 1899, **75**, 16; Carrière, *Ann. Chim.*, 1922, **17**, 38) is described as a liquid rapidly forming a solid trimer, m. p. 167°. By boiling this with aqueous alkali Carrière (*loc. cit.*) obtained an acidic product as its semicarbazone but was unable to isolate the parent acid. We have found that on being kept or on treatment with warm alkali as described by Carrière β-formylpropionic acid forms a polymeric substance, m. p. 184°, which depresses the melting point of the acidic compound, m. p. 191°. The product, m. p. 167°, was not observed.

The two nitrogenous metabolites (A), m. p. 159°, and (B), m. p. 146°, have the properties of saturated dibasic acids containing a hydroxamic acid residue and will be the subject of further investigation when sufficient material has been accumulated.

Experimental

Isolation of the Metabolic Products.—Cultures of the mould *Chaetomium indicum* Corda were maintained on slopes of glucose–peptone–agar. For production of the metabolites the organism was grown on liquid Czapek–Dox medium (sterile, with initial pH 4·2) at 30° for 22—24 days.

The filtered orange metabolic liquors (100 l.) were acidified (pH 1·0) with 10% sulphuric acid and 24 hr. later the resulting flocculent brown precipitate, which had settled, was collected and the aqueous filtrate concentrated in a "climbing-film" evaporator. After the addition of ammonium sulphate (1·5 kg.) the resulting concentrate (20—25 l.) was exhaustively extracted with ether in a counter-current extractor, and the gummy residue left on the evaporation of the dried extract was crystallised from hot chloroform (*ca.* 700 ml.). Repeated recrystallisation of the product from chloroform–light petroleum (b. p. 60—80°) then gave *4-carboxy-2-oxo-3-phenylhept-3-enedioic acid* (25—50 g.) in colourless, rectangular prisms containing chloroform of crystallisation which was removed on the steam-bath during 1 hr. The compound then had m. p. 170° (decomp.), $\lambda_{max.}$ 288 ($\log_{10}\varepsilon$ 4·25) and $\lambda_{min.}$ 237 ($\log_{10}\varepsilon$ 3·32) in EtOH [Found: C, 57·6; H, 4·2%; *M* (Rast), 291; equiv., by potentiometric titration, 97·4. $C_{14}H_{12}O_7$ requires C, 57·5; H, 4·1%; *M*, 292; equiv., for a tribasic acid, 97·3). This acid is moderately soluble in cold water and readily soluble in hot water and in the usual organic solvents except chloroform or light petroleum. It slowly dissolves in aqueous sodium hydrogen carbonate with the evolution of carbon dioxide.

Treatment of the acid (1 g.) dissolved in ether at 0° with an excess of ethereal diazomethane for 15 min. gave the *trimethyl ester* which was purified by being washed in ethereal solution with aqueous sodium hydrogen carbonate followed by distillation and obtained as a pale yellow viscous oil (1 g.), b. p. 187—189°/0·4 mm., insoluble in aqueous sodium hydroxide [Found: C, 61·5; H, 5·2; OMe, 26·0. $C_{14}H_9O_4(OMe)_3$ requires C, 61·6; H, 5·4; OMe, 27·8%].

The brown precipitate, obtained on acidification of the metabolic liquor, was extracted with light petroleum (b. p. 60—80°) and on concentration this extract deposited *substance* (A) in small, pale yellow needles which, after repeated purification from chloroform–light petroleum, had m. p. 159°, $[\alpha]_D^{20}$ +11·4° (*c*, 1·022 in $CHCl_3$), $\lambda_{max.}$ 286 ($E_{1\,cm.}^{1\%}$ 346) (yield, 1·5—2·0 g. from 100 l. of liquor) [Found, in specimen dried in a high vacuum at 70°: C, 67·7; H, 8·0; N, 3·1%; equiv. (potentiometrically), 231; *M* (Rast), 445. $C_{26}H_{37}O_6N$ requires C, 68·0; H, 8·1; N, 3·1%; equiv., 229·8; *M*, 459·6]. This compound, which readily dissolved in aqueous sodium hydrogen carbonate, gave a wine-red ferric reaction in alcohol and a highly insoluble green-blue copper derivative.

When a culture aged 18 months was employed for the production of 4-carboxy-2-oxo-3-phenylhept-3-enedioic acid, the brown precipitate contained in place of (A) smaller amounts of a *substance* (B) which was isolated and purified by the method employed for (A). Compound (B) separated from light petroleum (b. p. 60—80°) in small rosettes of colourless rectangular prisms, m. p. 146°, $[\alpha]_D^{20}$ +120° (*c*, 1·01 in $CHCl_3$), $\lambda_{max.}$ 287 ($E_{1\,cm.}^{1\%}$ 305) [Found, in specimen dried in a

high vacuum at 70° : C, 68·1; H, 8·2; N, 2·7; *C*-Me, 12·0%; equiv., 245·3; *M* (Rast), 482·8]. This compound had the same wine-red ferric reaction as (A) and formed an insoluble green copper derivative.

2-Oxo-3-phenylhept-3-enedioic Acid.—When a solution of (I) (2 g.) in 2N-sulphuric acid (50 ml.) was boiled in nitrogen for 2 hr. and then cooled, crystalline *2-oxo-3-phenylhept-3-enedioic acid* (1·4 g.) separated and, on purification from acetone–light petroleum (b. p. 60—80°), formed small colourless, rectangular prisms, m. p. 178°, $\lambda_{max.}$ 285 ($\log_{10}\varepsilon$ 4·35) and $\lambda_{min.}$ 233 ($\log_{10}\varepsilon$ 2·62) in EtOH, having an intense green ferric reaction in alcohol [Found : C, 62·5; H, 5·0%; *M* (Menzies–Wright), 245 in EtOH. $C_{13}H_{12}O_6$ requires C, 62·9; H, 4·9%; *M*, 248]. The same product (160 mg.) was formed by heating the parent acid (200 mg.) at 180° in a high vacuum and had m. p. and mixed m. p. 178° after purification from ether and then acetone–light petroleum. It is readily soluble in the usual solvents except water and light petroleum and dissolves slowly in aqueous sodium hydrogen carbonate.

When the effluent gases from the boiling sulphuric acid solution were led into aqueous barium hydroxide a precipitate of barium carbonate separated, whereas with aqueous 2 : 4-dinitrophenylhydrazine sulphate a precipitate was not formed.

Treatment of 2-oxo-3-phenylheptadienoic acid (1 g.) in a mixture of methanol (20 ml.) and ether (25 ml.) at 0° with an excess of ethereal diazomethane for 15 min. gave an oil. A solution of this in ether (25 ml.) was washed with aqueous sodium hydrogen carbonate, dried, and evaporated, leaving the *dimethyl* ester which slowly solidified and then separated from light petroleum (b. p. 40—60°) in rosettes of long, slender needles, m. p. 52—53°, insoluble in aqueous sodium hydroxide [Found : C, 65·5; H, 5·8; OMe, 21·2. $C_{13}H_{10}O_3(OMe)_2$ requires C, 65·2; H, 5·8; OMe, 22·5%]. This ester behaved as a saturated compound and failed to react with carbonyl reagents. The same ester (1 g.), m. p. and mixed m. p. 52—53°, was formed by esterification of the acid (1 g.) with methyl iodide (5 ml.) and potassium carbonate (7·5 g.) in boiling acetone (60 ml.) for 15 hr.

When a solution of this ester (1 g.) in methanol (15 ml.) was treated with 2N-aqueous sodium hydroxide (15 ml.) the initial precipitate rapidly dissolved and 5 min. later the mixture was acidified with concentrated hydrochloric acid, diluted with water (125 ml.), and extracted with ether (25 ml. × 3). The ethereal extracts were washed with 2N-sodium hydrogen carbonate (30 ml. × 3), and the washings acidified and extracted with ether. Evaporation of the combined, dried extracts left *methyl hydrogen 2-oxo-3-phenylhept-3-enedioate* which solidified on trituration with light petroleum (b. p. 60—80°), and then crystallised from the same solvent in rosettes of colourless needles (0·75 g.), m. p. 127—128°, having a negative ferric reaction (Found : C, 64·0; H, 5·2; OMe, 13·0. $C_{13}H_{11}O_4$·OMe requires C, 64·1; H, 5·4; OMe, 11·8%). Treatment of this compound with ethereal diazomethane regenerated the parent dimethyl ester, m. p. and mixed m. p. 52—53°.

Degradation of 4-carboxy-2-oxo-3-phenylhept-3-enedioic Acid with Aqueous Sodium Hydroxide.—A solution of the acid (1 g.) in 2N-sodium hydroxide was boiled in nitrogen for ½ hr., cooled, acidified with 2N-sulphuric acid, and extracted with ether in a continuous extractor for 20 hr. The semi-solid orange-red product left on evaporation of the ethereal extract was repeatedly extracted with boiling benzene, leaving an intractable residue (*ca.* 400—500 mg.). Concentration of the combined benzene extracts gave a crystalline product, part of which readily redissolved in a little hot benzene. On cooling, this solution deposited phenylpyruvic acid in colourless plates (250 mg.), m. p. 158°, identical with an authentic specimen and having an intense green ferric reaction (Found : C, 66·2; H, 5·0. Calc. for $C_9H_8O_3$: C, 65·9; H, 4·9%). The 2 : 4-dinitrophenylhydrazone separated from dilute alcohol in small yellow needles, m. p. 190—191°, identical with an authentic specimen (Found : C, 53·3; H, 3·6; N, 16·2. Calc. for $C_{15}H_{12}O_6N_4$: C, 52·3; H, 3·5; N, 16·3%).

The crystalline residue, sparingly soluble in hot benzene, was purified by repeated sublimation in a high vacuum and gave α-oxoglutaric acid in colourless needles, m. p. 115—116°, undepressed on admixture with an authentic specimen (Found : C, 41·1; H, 4·2. Calc. for $C_5H_6O_5$: C, 41·1; H, 4·1%). The 2 : 4-dinitrophenylhydrazone formed rosettes of yellow needles, m. p. 227° (decomp.), from dilute alcohol, identical with an authentic specimen (Found : C, 40·1; H, 3·4; N, 17·6. Calc. for $C_{11}H_{10}O_9N_4$: C, 40·5; H, 3·1; N, 17·2%).

When the alkaline hydrolysate (25 ml.) from the acid (500 mg.) was acidified, diluted with water, and treated with 2 : 4-dinitrophenylhydrazine (1 g.), and the precipitate was dissolved in concentrated sulphuric acid (25 ml.) and water (200 ml.), and heated on the steam-bath for 10 min., a yellow precipitate of the mixed 2 : 4-dinitrophenylhydrazones of phenylpyruvic acid and α-oxoglutaric acid was obtained. This was resolved by means of hot benzene, and the

components were identified by comparison with authentic specimens. When the acidified hydrolysate was diluted with water and distilled the distillate did not contain a volatile acid.

Oxidation of 4-Carboxy-2-oxo-3-phenylhept-3-enedioic Acid.—(*a*) 5% Aqueous potassium permanganate (50 ml.) was added dropwise to a solution of the acid (1 g.) in acetone (50 ml.) during ½ hr. and, after the mixture had been cleared with sulphur dioxide and the greater part of the acetone evaporated, the aqueous liquor was extracted continuously with ether for 12 hr. From the semi-crystalline product (0·6 g.) left on evaporation of the ethereal extract boiling light petroleum (b. p. 60—80°) extracted benzoic acid (0·4 g.), m. p. and mixed m. p. 122°, after crystallisation from water and sublimation at 100—110°/2·4 mm.

The residue, insoluble in light petroleum, was triturated with a little chloroform and then crystallised from acetone–light petroleum (b. p. 60—80°), giving succinic acid in colourless needles (0·1 g.), m. p. and mixed m. p. 185° (Found: C, 41·3; H, 5·1. Calc. for $C_4H_6O_4$: C, 40·7; H, 5·1%). The *p*-toluidide had m. p. and mixed m. p. 262—263° (Found: N, 9·7. Calc. for $C_{18}H_{20}O_2N_2$: N, 9·5%).

The same products were formed when the acid was oxidised in 4% aqueous sodium hydrogen carbonate.

(*b*) A solution of the acid (1 g.) in 2N-sodium hydroxide (20 ml.), containing hydrogen peroxide (3 ml. of 100-vol.), was kept for 72 hr., acidified, and continuously extracted with ether for 72 hr. The product left on evaporation of the ethereal extract was resolved into benzoic (0·2 g.) and succinic acid (150 mg.) by the method employed in (*a*).

(*c*) A moderate stream of ozone and oxygen was led into a solution of the acid (1 g.) in ethyl acetate (75 ml.) at 0° for 1 hr., the solvent evaporated in a vacuum, and the residue dissolved in water containing manganese dioxide (200 mg.). After 12 hr. the mixture was heated on the steam-bath for 40 min., cooled, and extracted with ether. Evaporation of the extracts left a mixture of benzoic (30 mg.) and succinic acid (100 mg.). The presence of volatile acids or carbonyl compounds could not be detected.

When the ozonide was decomposed with a solution of 2 : 4-dinitrophenylhydrazine (1 g.) in concentrated sulphuric acid (25 ml.) and water (200 ml.) a red-orange gummy solid (0·5 g.) separated which was collected after 18 hr., dried, and extracted with hot benzene. The 2 : 4-dinitrophenylhydrazone of α-oxoglutaric acid was obtained from the extract and on purification from aqueous alcohol and then ethyl acetate–light petroleum (b. p. 60—80°) had m. p. 227° (decomp.), identical with an authentic specimen (Found: N, 17·6. Calc. for $C_{11}H_{10}O_8N_4$: N, 17·2%).

Degradation of 2-Oxo-3-phenylhept-3-enedioic Acid.—(*a*) This acid (1 g.) was boiled with 2N-aqueous sodium hydroxide (50 ml.) in nitrogen for ½ hr. and the cooled, acidified liquor extracted with ether in a continuous extractor. A small amount of a colourless substance (100 mg.) separated from the ethereal extract and on recrystallisation from acetone–light petroleum (b. p. 60—80°) formed small colourless needles, m. p. 191°, having a negative ferric reaction (Found: C, 55·4; H, 5·5%). After the removal of this compound evaporation of the ether gave phenylpyruvic acid, having m. p. 158° on purification from benzene (Found: C, 65·8; H, 5·0. Calc. for $C_9H_8O_3$: C, 65·9; H, 4·9%). The 2 : 4-dinitrophenylhydrazone had m. p. and mixed m. p. 191—192°.

(*b*) 5% Aqueous potassium permanganate (50 ml.) was added dropwise to a solution of the acid (1 g.) in acetone during ½ hr., the mixture cleared with sulphur dioxide, the acetone evaporated, and the residue extracted with ether. The product from the ethereal extracts was separated into benzoic acid (0·4 g.) (soluble) and oxalic acid (50 mg.) (insoluble) [by means of hot light petroleum (b. p. 60—80°)] which were purified and identified respectively by comparison with authentic specimens.

(*c*) Oxidation of the acid (1 g.) in 2N-sodium hydroxide (20 ml.) with hydrogen peroxide (3 ml. of 100-vol.) at room temperature for 72 hr. followed by extraction of the acidified mixture with ether gave benzoic acid (400 mg.) and succinic acid (150 mg.).

(*d*) Ozonolysis of this acid by the procedure employed in the case of (I) gave a mixture of succinic and benzoic acid. Volatile acidic or carbonyl compounds could not be detected.

When the ozonide from the acid (1 g.) was decomposed with a solution of 2 : 4-dinitrophenylhydrazine (1 g.) in concentrated sulphuric acid (25 ml.) and water (200 ml.), purification of the resulting yellow precipitate from aqueous alcohol and then ethyl acetate–light petroleum (b. p. 60—80°) gave the 2 : 4-*dinitrophenylhydrazone* of β-formylpropionic acid in orange-yellow needles (0·3 g.), m. p. 202—203° (Found: C, 42·9; H, 3·7; N, 19·8. $C_{10}H_{10}O_6N_4$ requires C, 42·6; H, 3·6; N, 19·9%). On being kept the aqueous liquors deposited a further quantity of this derivative (0·15 g.).

(*e*) When the monomethyl ester of 2-oxo-3-phenylhept-3-enedioic acid (1 g.) was ozonised in methyl acetate at 0° and the oily ozonide decomposed with a cold solution of 2 : 4-dinitrophenylhydrazine sulphate (1 g.) in concentrated sulphuric acid (25 ml.) and water (200 ml.), the 2 : 4-dinitrophenylhydrazone (0·3 g.) of β-formylpropionic acid was obtained. This had m. p. 203° and was identical with an authentic specimen.

Prepared from authentic β-formylpropionic acid (Carrière, *Ann. Chim.*, 1922, **17**, 38), the 2 : 4-dinitrophenylhydrazone formed orange-yellow needles, m. p. 202—203°, from ethyl acetate–light petroleum (Found : C, 42·4; H, 3·8; N, 19·6%).

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494. *The Chemistry of Fungi. Part XXI.* Asperxanthone and a Preliminary Examination of Aspergillin.*

By N. A. LUND, ALEXANDER ROBERTSON, and W. B. WHALLEY.

Isolated from several varieties of *Aspergillus niger*, the black amorphous pigment aspergillin has been obtained free from iron and nitrogenous material. On oxidation with hydrogen peroxide aspergillin gave small yields of acetaldehyde, oxalic acid, and mellitic acid; the two acids were also formed with potassium permanganate. Nitric acid gave the same three products along with a little picric acid.

From the mycelium of several strains of *A. niger* there have been isolated small amounts of a new 1-hydroxydimethoxymethylxanthone, asperxanthone $C_{13}H_5O_3(OMe)_2Me$, which on demethylation gave nor-rubrofusarin. Comparison of the ultra-violet absorption spectrum of asperxanthone with the spectra of a number of synthetic polyhydroxyxanthones did not assist in the location of the substituents in the new xanthone.

AN examination of the well-known black pigment aspergillin produced by varieties of *Aspergillus niger* was undertaken as part of a comprehensive study of melanin-like pigments of plants and animals in progress in these laboratories. The first recorded isolation of this substance appears to have been made by Linossier (*Compt. rend.*, 1891, **112**, 489) who extracted the spores of *A. niger* with aqueous ammonia, obtaining the pigment by acidification of the extracts. On slender evidence, chiefly because he obtained ferric oxide on ignition of this product, which he named aspergillin,† Linossier concluded that it was analogous in nature and function to hæmatin, a view which he reaffirmed later (*ibid.*, 1891, **112**, 807; 1910, **151**, 1075) without presenting further experimental evidence. Hugouenq and Florence (*Bull. Soc. Chim. biol.*, 1920, **2**, 133) isolated aspergillin with aqueous sodium hydroxide and re-precipitated it from ammonia, obtaining a product which gave the following analytical results: C, 47·3; H, 7·2; N, 11·4; Ash, 5·0%. On the basis of its physical characteristics Bortels (*Biochem. Z.*, 1927, **182**, 301) concluded that aspergillin was probably identical with the humic acid of peat whilst Rippel and Walter (*ibid.*, 1927, **186**, 474) considered it to be a nitrogen-containing pigment of the melanin type. In a more systematic examination of the substance Quilico and de Capua (*Atti R. Accad. Lincei*, 1933, **17**, 93, 197; *Gazzetta*, 1933, **63**, 400) obtained material containing 0·35% of iron which they suggested was a constituent part of the molecule. By oxidation of the pigment these authors obtained mellitic acid and oxalic acid and quoted examples indicating an analogy between these results and those obtained from oxypyrrole blacks, melanins, and humic acid. They noted, however, that nitrogen may not be an essential constituent and suggested that the compound was similar to humic acid and the polymeric oxidation products of phenols. The relationship to humic acid was supported by the similarity of

* Part XX, preceding paper.

† The trivial name aspergillin has been applied since to other products from *Aspergilli* by Stanley (*Australian J. Sci.*, 1944, **6**, 151; *Australian J. Exp. Med. Sci.*, 1946, **24**, 133), Korenyako and Krasil'nikov (*Microbiologia, U.S.S.R.*, 1945, **14**, 347), Soltys (*J. Path. Bact.*, 1946, **58**, 278), and Kovalev (*Veterinaviya*, 1940, **25**, 40), but since this black pigment has invariably been referred to as aspergillin and the name has precedence we propose that it should be retained (cf. Tobie, *Nature*, 1946, **158**, 709).

the *X*-ray patterns obtained from the two compounds (Quilico and Rollier, *Chem. Abs.*, 1939, **33**, 8074, 8467).

In the present work aspergillin was isolated with alkali from several strains of *Aspergillus niger* and purified by a number of procedures. Dialysis followed by electrodialysis removed the greater part of the mineral constituents of the crude pigment, reducing the iron content from about 2% to 0·012%. Subsequently it was found that extraction of the crude aspergillin with hot water removed a mucilaginous polysaccharide and that treatment of the product with hot dilute sulphuric acid then gave a pigment free from nitrogen and iron. This was then digested with boiling methanol. When thus purified, aspergillin is a black, amorphous, acidic compound, having the properties of a cross-linked polymer and closely resembling humic acid, the inorganic constituents of which Pluguian and Hibbert (*J. Amer. Chem. Soc.*, 1935, **57**, 528) regard as impurities only. In agreement with the observations of Quilico *et al.* (*loc. cit.*) oxidation of aspergillin gave mellitic and oxalic acid but in addition small amounts of acetaldehyde were formed, whilst nitric acid also produced a little picric acid. The relationship of the purified pigment to humic acid has been further substantiated by a comparison of its infra-red spectrum with that of humic acid (Cannon and Sutherland, *Trans. Faraday Soc.*, 1945, **41**, 279).

The nitrogen content of crude aspergillin, which shows considerable variation, appears to be due to a protein-like component but whether this and the polysaccharide-like material are chemically bound to the pigment residue is not yet clear. The variation in nitrogen content and the ease with which the polysaccharide is eluted indicates that they are present as impurities.

Asperxanthone.—On extraction with methanol the defatted mycelium of *A. niger* N.R.R.L. 67, *A. niger* Van Tieghem 9029, and two strains of unknown origin gave, in addition to a little mannitol, a crystalline phenolic product in very low yield. This compound contains two methoxyl groups, a *C*-methyl group, and a hydroxyl group in the *o*-position to a carbonyl group. From the empirical formula $C_{13}H_5O_3(OMe)_2Me$ in conjunction with its general properties, including the absence of a reactive carbonyl group, the stability to warm acids and alkalis, and the formation of an unstable perchlorate and a diacetoborate, the phenol appeared to be a new 1-hydroxydimethoxymethylxanthone. On demethylation it furnished a trihydroxyxanthone; the ultra-violet absorption spectrum curve of this was practically identical with that recorded for nor-rubrofusarin, the orientation of which has not been determined (Mull and Nord, *Arch. Biochem.*, 1944, **4**, 419). With a small sample of nor-rubrofusarin kindly supplied to us by Professor Nord, the respective ultra-violet absorption spectra of the two compounds have been determined with a " Unicam " spectrograph used in this laboratory (cf. *Ann. Reports*, 1951, **48**, 347) and found to be almost identical. Further, as a mixture of the two products did not show a depression in the decomposition point it seems reasonably certain that they are identical, *i.e.*, the new xanthone is a nor-rubrofusarin dimethyl ether, which for convenience we have provisionally named asperxanthone.

As didemethylasperxanthone (nor-rubrofusarin) was not identical with the readily synthesised 1 : 5 : 6-, 1 : 6 : 7-, or 1 : 6 : 8-trihydroxy-3-methylxanthone and because the quantity of the compound available was insufficient for degradation experiments, attempts were made to deduce the position of the second and third hydroxyl groups from an examination of the ultra-violet absorption spectra of a number of hydroxyxanthones. Accordingly, the spectra of asperxanthone and nor-rubrofusarin have been compared with those of 1-, 2-, 3-, and 4-hydroxyxanthone, 1-hydroxy-5-methylxanthone, 1 : 3-, 1 : 6-, and 1 : 8-dihydroxyxanthone, 1 : 5- and 1 : 7-dihydroxy-3-methylxanthone, ravenelin (Raistrick, Robinson, and White, *Biochem. J.*, 1936, **30**, 1303), and 1 : 6 : 7- and 1 : 6 : 8-trihydroxy-3-methylxanthone. From an analysis of these results it has not been possible to establish a correlation between the ultra-violet spectra and the position of the hydroxyl groups. In this connection it would appear that the tentative structure assigned to nor-rubrofusarin by Mull and Nord (*loc. cit.*) based on the examination of the absorption spectra of a limited number of hydroxyxanthones is open to doubt.

The syntheses of 1 : 3 : 5- and 1 : 3 : 6-trihydroxyxanthone, 1 : 5-dihydroxy-3-methylxanthone, 1 : 3 : 5- and 1 : 3 : 6-trihydroxyxanthone, and 1 : 5 : 6-, 1 : 6 : 7-, and 1 : 6 : 8-

trihydroxy-3-methylxanthone have been effected by the application of Michael's method (*Amer. Chem. J.*, 1883, **5**, 81) as used by Kostanecki and his collaborators for the preparation of numerous substituted xanthones (see, *e.g.*, *Ber.*, 1891, **24**, 1896) in which equimolecular proportions of the requisite phenol and phenolic acid are heated with a dehydrating reagent, usually acetic anhydride. In the present work it has been found that optimum results are obtained when the amount of anhydride employed is that required to abstract two molecular proportions of water and when the amount of reactants employed did not exceed the 0·05-molar scale.

Experimental

Isolation of Aspergillin.—From pilot experiments with six strains of *Aspergillus niger*, *viz.*, *A. niger* van Tieghem **9029**, *A. niger* van Tieghem **330**, *A. niger* van Tieghem **32**, *A. niger* N.R.R.L. 67, and two strains of unknown origin it was found that *A. niger* van Tieghem 9029 gave the best yield of black pigment, and it was employed in the present work; the pigments obtained from the remaining five species were indistinguishable from aspergillin of *A. niger* van Tieghem 9029. Experiments with a number of liquid media with varying times of incubation show but little variation in the yield, although the following conditions appeared consistently to be slightly superior and were adopted. A modification of the sporulation medium described by Moyer, Wells, Stubbs, Kerrick, and May (*Ind. Eng. Chem.*, 1937, **29**, 777), *viz.*, glucose (91·3 g.), ammonium nitrate (0·45 g.), potassium dihydrogen phosphate (0·072 g.), hydrated magnesium sulphate (0·06 g.), and ferrous sulphate (0·01 g.), dissolved in water (1 l.), in standard " penicillin " flasks (in batches of 1000 flasks), each containing 1 l. of liquid medium, was inoculated with mould spores in the usual manner and incubated at 30° for 14 days. The mycelium was collected, drained for 24 hr., and then treated as follows.

(*a*) The mycelial felts from 500 flasks were kept in 1·5% aqueous sodium hydroxide (20 l.) with frequent vigorous agitation for 14 days, and the liquor was decanted through a large Buchner funnel (the slimy residue was pressed to remove as much solution as possible) and then clarified by filtration through muslin gauze and then through a sintered-glass (No. 3) funnel. Acidification of the resulting clear black liquid with 4% hydrochloric acid (8 l.) gave a black precipitate which slowly settled in the clear, yellow liquor, the greater part of which was siphoned off. On isolation the slimy product, which had been washed with water until the washings were free from chloride ion, was extracted with several portions of boiling methanol (each 1 l.) to remove small amounts of methanol-soluble products, giving a black amorphous solid (126 g.). Extraction of the mycelial felt with 2% aqueous ammonia gave a similar product.

(*b*) The air-dried, powdered mycelium (1 kg.) was extracted successively with light petroleum (b. p. 60—80°), and hot methanol, and then treated with 1·5% aqueous sodium hydroxide as in (*a*). The fine suspension obtained on acidification of the extract was collected by means of a Sharples supercentrifuge at 24,000 r.p.m., repeatedly washed until free from chloride ion, and collected in the same manner as above; the yield of air-dried product was *ca.* 10 g. The same final product was obtained when the extraction with alkali was carried out in an atmosphere of nitrogen.

After repeated extraction with alkali the mycelial residue still contained much black pigment which appeared to be insoluble.

Purification of the Pigment.—(a) *Removal of inorganic impurities.* Portions of freshly precipitated pigment were dialysed in collodion or Cellophane containers against running tap-water and then distilled water with reduction of the ash content. The product was then subjected to electrodialysis against distilled water. After 34 hr. the full working voltage of 300 v was necessary to maintain a current of 30 milliamp. and after a further period (30 hr.) the current passing, which had then fallen to 3 milliamp., was not reduced by continued application of the full voltage. The aspergillin was then collected, extracted with methanol, and dried, being obtained as a black hygroscopic powder, m. p. $>350°$. Four preparations of crude aspergillin having an average ash content of 1·995% and iron content of 0·203% had, on dialysis followed by electrodialysis, an ash content of 0·343% and an iron content of 0·030%.

(b) *Removal of nitrogen-containing compounds.* When aspergillin (3 g.) was heated under reflux with 12% hydrochloric acid (100 ml.) for 1½ hr. the cooled filtered hydrolysate reduced Fehling's and Molisch's reagents and gave a positive ninhydrin reaction but did not contain purine bases or phosphates. With phenylhydrazine it gave phenylglucosazone.

Extraction of crude aspergillin (100 g.) with boiling water gave a greyish gelatinous pre-

cipitate (1 g.) which, on purification from hot water, was obtained as a white powder soluble in 2N-sodium hydroxide and in hot water. This product which did not give a colour with iodine was hydrolysed with boiling 4% sulphuric acid, giving an almost quantitative yield of a reducing sugar which was isolated as phenylglucosazone. The identity of the latter was confirmed by the preparation of phenylglucosotriazole (Hahn and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 735), m. p. and mixed m. p. 195—196°.

After the foregoing experiments it was found that crude aspergillin (containing polysaccharide-like material *ca.* 1% and nitrogen *ca.* 3·87%) was conveniently purified thus: The freshly isolated crude pigment (20 g.) was extracted (Soxhlet) with water for 8 hr. to remove the polysaccharide-like material and then dissolved in 2% aqueous sodium hydroxide (250 ml.) and reprecipitated with 2% sulphuric acid. The pigment was collected, well washed, and heated under reflux with 20% sulphuric acid (150 ml.) for 20 hr.; the nitrogen content was thereby reduced to 1·95%. Repetition of this process gave a nitrogen-free product which was then extracted with boiling methanol (Found, in specimen dried at room temperature over phosphoric oxide for 24 hr.: C, 58·5; H, 4·1; N, nil; *C*-methyl, 3·49; Ash, 0·06; Fe, 0·007%). Thus purified, aspergillin (air-dried) is a jet-black powder which is readily soluble in aqueous sodium hydrogen carbonate. On being dried in a vacuum at room temperature it becomes hygroscopic and then dissolves slowly in aqueous sodium hydroxide or sodium hydrogen carbonate. Both undried and dried material are insoluble in the usual organic solvents, but are soluble or are dispersed in liquid ammonia, and in molten catechol, resorcinol, salicylic acid, or pyrogallol, sparingly soluble (or dispersed by) molten quinol or *p*-hydroxybenzoic acid, and insoluble in liquid sulphur dioxide, anisole, furfuraldehyde, benzyl alcohol, molten phenol, *o*-, *m*-, or *p*-cresol, guaiacol, benzoic acid, or camphor. The infra-red absorption spectrum of the pigment as a paste with liquid paraffin and hexachlorobutadiene was determined over the region 2—15 μ. As is usual with compounds of high molecular weight the absorption bands noted were not very strong. The following bands observed may be attributed with reasonable confidence as follows: 3·1 μ bonded O–H; 3·5 μ C–H; 5·9 μ C:O as in CO_2H; 6·1 μ benzenoid ring structure.

Oxidation of Aspergillin.—(*a*) Aspergillin (5 g.) was added to 5N-nitric acid (100 ml.) containing urea (2 g.), and the stirred mixture kept at 60° for 1 hr. Next day the black insoluble residue was removed, the liquor was neutralised with 2N-ammonia and treated with an excess of silver nitrate, and the precipitate (1 g.) was collected, washed, dried, and boiled with saturated methanolic hydrogen chloride (20 ml.) for ½ hr. The residue (90 mg.) left on evaporation of the filtered methanolic solution was treated with excess of ethereal diazomethane and on distillation the product gave methyl oxalate (7 mg.), b. p. 90°/30 mm., m. p. 51°, and hexamethyl mellitate (15 mg.), b. p. 160°/0·01 mm., m. p. and mixed m. p. 188°, after purification from methanol (Found: C, 51·0; H, 4·2. Calc. for $C_{18}H_{18}O_{12}$: C, 50·7; H, 4·3%).

When the oxidation was effected with 50% nitric acid and the mixture kept at 95—100°, the distillate contained acetaldehyde which was converted into the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 158° (yield, 50 mg., from 20 g. of pigment). From the acidic residue oxalic acid was isolated as calcium oxalate, and then mellitic acid as the silver salt which was converted into hexamethyl mellitate. After the removal of the silver salt the aqueous liquor was repeatedly extracted with benzene and on evaporation the dried benzene extracts left a little picric acid which was isolated as quinoline picrate in red needles, m. p. 202°, alone or admixed with an authentic specimen.

(*b*) Hydrogen peroxide (60 ml.; 50-vol.) was added to a solution of aspergillin (1·5 g.) in 0·2N-sodium hydroxide (100 ml.) during 3 hr.; the reacting mixture was kept at below 40°. 15 Hours later the solution was neutralised with nitric acid and, after the removal of the excess of hydrogen peroxide with manganese dioxide, was treated with silver nitrate, giving a precipitate from which methyl oxalate (7 mg.) and hexamethyl mellitate (0·12 g.) were obtained in the usual manner.

Oxidation of aspergillin with hydrogen peroxide according to the procedure of Quilico and de Capua (*loc. cit.*) or a number of modifications of this method failed to yield a residue of mellitic acid on distillation of the reaction mixture. The distillate contained acetaldehyde, isolated as the 2 : 4-dinitrophenylhydrazone.

(*c*) Oxidation of aspergillin (3 g.), dissolved in 0·5N-sodium hydroxide (300 ml.), with potassium permanganate (8 g. in 150 ml. of water) on the steam-bath for ½ hr. gave an acidic product from which methyl oxalate (0·47 g.) and hexamethyl mellitate (1·2 g.) were isolated by way of their silver salts.

Asperxanthone.—The dried pulverised mycelium of *Aspergillus niger* (1 kg.) was extracted

(Soxhlet) with light petroleum (b. p. 60—80°) for 100 hr. and then with methanol for 150 hr. Concentration of the methanolic extract gave mannitol, m. p. 166°, after purification, identified by comparison with an authentic specimen. On evaporation the residual liquor then gave a black viscous product (45 g.) which was repeatedly extracted with ether. After having been washed with 0·5N-sodium hydroxide (300 ml. × 2), the combined ethereal extracts were evaporated, leaving a yellow amorphous residue (2 g.) which on repeated crystallisation from chloroform–alcohol gave *asperxanthone* in primrose-yellow needles (450 mg.), m. p. 203°, unchanged on sublimation in a high vacuum [Found: C, 67·2; H, 5·0; OMe, 21·7; *C*-Me, 5·6. $C_{13}H_5O_3(OMe)_2Me$ requires C, 67·1; H, 4·9; OMe, 21·7; *C*-Me, 5·3%]. This compound, which gives an intense green ferric reaction in alcohol, is readily soluble in alcohol or ether, insoluble in light petroleum, and dissolves with difficulty in 2N-sodium hydroxide, forming a yellow solution from which it is precipitated unchanged with acid. With warm perchloric and acetic acid asperxanthone gave an unstable perchlorate in bright yellow needles, m. p. 270° (decomp.), and with boroacetic anhydride in acetic anhydride a yellow boroacetate, m. p. 210—220° (decomp.), which, on treatment with warm water, regenerated the parent compound. Demethylated with hydriodic acid (10 ml; *d* 1·7) at 100° for 5 hr. asperxanthone (200 mg.) gave a product which separated from methanol in orange-yellow needles (100 mg.), m. p. 286—290° after darkening at 240°, undepressed on admixture with nor-rubrofusarin (*loc. cit.*); it sublimed unchanged at 200°/0·001 mm. (Found: C, 64·7; H, 4·2. Calc. for $C_{14}H_{10}O_5$: C, 65·1; H, 3·9%). This compound, which is readily soluble in alcohol and insoluble in water, gives an intense green-brown ferric reaction in alcohol and forms a deep yellow solution with aqueous sodium hydroxide which slowly becomes brown in air. Prepared by warm pyridine–acetic anhydride at 100° for 5 hr., the *triacetate* separated from acetic acid and then alcohol in deep golden-yellow needles, m. p. 210°, having a negative ferric reaction (Found: C, 62·3; H, 4·4. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%).

1 : 6 : 8-*Trihydroxy*-3-*methylxanthone*.—A mixture of *p*-orsellinic acid (Robertson and Robinson, *J.*, 1927, 2199) (2·1 g.), phloroglucinol (1·55 g.), and acetic anhydride (3 ml.) was gradually heated to 200° and the distillate discarded. The residue was then distilled in a vacuum and the fraction, b. p. 270—290°/0·5 mm., obtained as a yellow glass, was dissolved in ether. Extraction of this solution with 2N-sodium hydroxide, followed by acidification of the extract, gave a product from which **1 : 6 : 8-*trihydroxy*-3-*methylxanthone*** was separated with hot ether. Crystallised from 95% alcohol this xanthone formed pale cream-coloured needles (2·6 g.), m. p. 275° (decomp.), moderately soluble in benzene, chloroform, or ether and having an intense brown ferric reaction (Found: C, 65·2; H, 3·6. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%). The *triacetate* separated from dilute acetic acid in colourless silky needles, m. p. 204°, with a negative ferric reaction (Found: C, 62·6; H, 4·2. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%).

1 : 5 : 6-*Trihydroxy*-3-*methylxanthone*.—Distillation of a mixture of *p*-orsellinic acid (2·1 g.), pyrogallol (1·55 g.), and acetic anhydride (3 ml.) yielded a primrose-yellow solid, b. p. 160—200°/0·5 mm. which, on being washed with ether and then crystallised from chloroform–alcohol, gave **1 : 5 : 6-*trihydroxy*-3-*methylxanthone*** in primrose-yellow needles (0·83 g.), m. p. 243°, having solubilities similar to those of **1 : 6 : 8**-trihydroxy-3-methylxanthone and an intense green ferric reaction (Found: C, 63·4; H, 3·6%). The *triacetate* formed colourless needles, m. p. 178°, from alcohol (Found: C, 62·9; H, 4·1%).

1 : 3 : 6-*Trihydroxyxanthone*.—Prepared by the standard method from β-resorcylic acid (1·54 g.), phloroglucinol (1·28 g.), and acetic anhydride (3 ml.), the fraction, b. p. 160—260°/0·5 mm., was dissolved in ether, and the solution repeatedly extracted with 2N-sodium hydroxide. Acidification of the combined extracts gave **1 : 3 : 6-*trihydroxyxanthone*** which was purified from pyridine, forming mustard-yellow needles (0·5 g.), m. p. 332° (decomp.), unchanged on sublimation at 220°/0·01 mm., with a red-brown ferric reaction (Found: C, 63·7; H, 3·5. $C_{13}H_8O_5$ requires C, 63·9; H, 3·3%). This compound is almost insoluble in alcohol, acetone, benzene, dioxan, or ethyl acetate. The *triacetate* separated from acetic acid or alcohol in colourless needles, m. p. 160° (Found: C, 61·7; H, 3·9. $C_{19}H_{14}O_8$ requires C, 61·6; H, 3·8%).

1 : 5-*Dihydroxy*-3-*methylxanthone*.—An intimate mixture of *p*-orsellinic acid (830 mg.), catechol (550 mg.), and phosphoric oxide (1 g.) was kept at 200° for 5 min. and poured into water (150 ml.). Sublimation of the resulting yellow precipitate at 190°/0·001 mm. followed by recrystallisation of the sublimate from ethanol gave **1 : 5-*dihydroxy*-3-*methylxanthone*** in primrose-yellow needles (300 mg.), m. p. 264°, with a green ferric reaction (Found: C, 69·8; H, 4·4. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·2%). The *diacetate* formed colourless needles, m. p. 142°, from alcohol (Found: C, 66·2; H, 4·3. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%).

1-*Hydroxy*-6 : 7-*dimethoxy*-3-*methylxanthone*.—Distillation of a mixture of **3 : 4**-dimethoxy-

phenol (Baker and Evans, *J.*, 1938, 375) (7·7 g.), *p*-orsellinic acid (9·3 g.), and acetic anhydride (15 ml.) gave a fraction, b. p. 200—250°/10 mm., which, on being washed with ether and crystallised from alcohol, furnished **1-*hydroxy*-6 : 7-*dimethoxy*-3-*methylxanthone*** in colourless needles (30 mg.), m. p. 204°, with a greenish-brown ferric reaction (Found : C, 67·0; H, 4·8. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). On demethylation with warm hydriodic acid this ether (20 mg.) gave 1 : 6 : 7-trihydroxy-3-methylxanthone which was purified by sublimation at 180°/0·1 mm. and obtained in primrose-yellow needles (5 mg.), m. p. >300°, with a greenish-brown ferric reaction.

1 : 3 : 5-*Trihydroxyxanthone*.—Prepared from 2 : 3-dihydroxybenzoic acid (9·24 g.), phloroglucinol (7·66 g.), and acetic anhydride (12 ml.) this *xanthone* (950 mg.) (from the fraction, b. p. 260—280°/0·1 mm.) was crystallised from dilute alcohol and sublimed at 170°/0·1 mm., being obtained in pale yellow needles, m. p. 255°, with a red-brown ferric reaction (Found : C, 63·3; H, 3·5%). The *triacetate* separated from alcohol in colourless needles, m. p. 204° (Found : C, 61·6; H, 3·8%).

5 : 8′-*Dihydroxy*-6 : 7′-*dimethylchromono*(2′ : 3′ : 2 : 3)*xanthone*.—Distillation of a mixture of quinol (5·5 g.), *p*-orsellinic acid (8·4 g.), and acetic anhydride (12 ml.) gave a distillate consisting of pale yellow needles with a little colourless oil. This was washed with ether and the yellow residue (450 mg.) purified by sublimation at 200°/0·01 mm., giving the ***chromonoxanthone*** in pale yellow needles, m. p. 209—210°, sparingly soluble in the usual organic solvents and having an intense green ferric reaction (Found : C, 70·7; H, 4·1. $C_{22}H_{14}O_6$ requires C, 70·6; H, 3·8%). The diacetate separated from alcohol in colourless leaflets or from acetic acid in colourless needles, m. p. 226°.

[With D. H. Johnson] **2-*Hydroxy*-6-*methoxybenzonitrile*.**—The following improved methods were employed for the preparation of this nitrile required for the synthesis of ravenelin according to the method of Raistrick *et al.* (*loc. cit.*). (*a*) Methyl 3-formyl-2 : 4-dihydroxybenzoate (Shah and Laiwalla, *J.*, 1938, 1828) (2 g.) was hydrolysed with boiling 30% aqueous potassium hydroxide (40 ml.) in nitrogen for 5 hr. On isolation in the usual manner an ethereal solution of the product was washed with 2N-sodium hydrogen carbonate, dried, and evaporated, leaving γ-resorcylaldehyde (1 g.), m. p. 154°, after purification from warm water (cf. Shah and Laiwalla, *loc. cit.*, who give m. p. 155—156°). Methylation of this aldehyde (6 g.) with methyl sulphate (5·5 g.) and potassium carbonate (12 g.) in boiling acetone (40 ml.) for 6 hr. gave 2-hydroxy-6-methoxybenzaldehyde, forming pale yellow needles (5 g.), m. p. 75°, from aqueous methanol (cf. Limaye, *Rasayanam*, 1936, **1**, 1). This aldehyde was converted into 2-hydroxy-6-methoxybenzonitrile by the method of Mull and Nord (*loc. cit.*).

(*b*) When a mixture of 2-hydroxy-6-methoxyacetophenone (Baker, *J.*, 1939, 956) (1·45 g.), iodine (2·21 g.), and pyridine (10 ml.) was heated on the steam-bath for 1 hr. and then kept at 0° for 16 hr., 1-(2-hydroxy-6-methoxyphenacyl)pyridinium iodide separated in massive prisms. A solution of this in a little hot alcohol was added to 2% aqueous potassium hydroxide (75 ml.), and the mixture heated on the steam-bath in nitrogen for 1 hr., cooled, and acidified with hydrochloric acid, giving 2-hydroxy-6-methoxybenzoic acid in colourless needles (850 mg.), m. p. 135°, after purification (cf. Clewer, *J.*, 1915, **107**, 839). This acid was converted into the nitrile by way of the amide according to standard procedures.

The infra-red absorption spectrum of aspergillin was determined by courtesy of Imperial Chemical Industries Limited, General Chemical Division, Widnes. One of us (N. A. L.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

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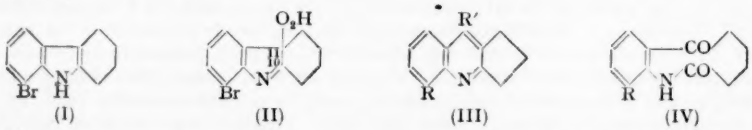
495. *Peroxides of Tetrahydrocarbazole and Related Compounds. Part V.* 8-Bromo-1 : 2 : 3 : 4-tetrahydrocarbazole.*

By R. J. S. Beer, T. Broadhurst, and Alexander Robertson.

From an examination of 8-bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl hydroperoxide (II) and its transformation products it appears that the compounds (A), (B), and (C) which Barnes, Pausacker, and Badcock (*J.*, 1951, 730) considered to be formed along with 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole in the Fischer indole synthesis are the hydroperoxide (II), the lactam of δ-(2-amino-3-bromobenzoyl)-*n*-valeric acid, and 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline.

By the cyclisation of *cyclo*hexanone *o*-bromophenylhydrazone according to the standard Fischer method Barnes, Pausacker, and Badcock (*J.*, 1951, 730) obtained the expected 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole (I) together with three undentified compounds, (A) $C_{12}H_{10}O_2NBr$, (B) $C_{12}H_{10}O_2NBr$, and (C) $C_{12}H_8ONBr$, which they suggested might be derived from the *o*-bromanilino-radical regarded as an intermediate in the Fischer indole cyclisation according to the mechanism proposed by Pausacker and Schubert (*J.*, 1949, 1384). It seemed to us that peroxidation of (I) was likely to take place under the conditions employed for the isolation of the carbazole (I) and the accompanying products (A), (B), and (C). On the view that (A) is 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide, $C_{12}H_{12}O_2NBr$ (II), and that (B) and (C) are artefacts derived from it a reasonably complete interpretation of the data given by Barnes and his co-workers is possible. Thus (C) is obtained by the action of alkali on (A) under conditions whereby tetrahydrocarbazolyl hydroperoxides are converted into 4-hydroxy-2 : 3-*cyclo*pentenoquinolines (cf., *e.g.*, Part IV*) and can be formulated as 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline (III; R = Br, R′ = OH). Further, the properties of the amphoteric compound $C_{12}H_{11}ON$, formed by the reductive debromination of (C), closely resemble those of 4-hydroxy-2 : 3-*cyclo*pentenoquinoline (III; R = H; R′ = OH) (Part II, *J.*, 1950, 3283), whilst the basic reduction product $C_{12}H_{11}N$, m. p. 60°, from (C) can be identified as 2 : 3-*cyclo*pentenoquinoline (III; R = R′ = H), m. p. 59—60° (Borsche, *Annalen*, 1910, **377**, 120).



In confirmation of the foregoing hypothesis the hydroperoxide (II) was prepared from (I) by the usual method (cf. Part IV) and on treatment with cold aqueous sodium hydroxide was smoothly converted into 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline (III; R = Br, R′ = OH) which was readily debrominated by hydrogenolysis, giving 4-hydroxy-2 : 3-*cyclo*pentenoquinoline (III; R = H, R′ = OH). By the vigorous catalytic reduction procedure employed by Barnes *et al.* 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline gave rise to small amounts of (III; R = H, R′ = OH) in addition to 2 : 3-*cyclo*pentenoquinoline (III; R = R′ = H), an authentic specimen of which was prepared by the reductive dechlorination of (III; R = H, R′ = Cl) (cf. Borsche, *loc. cit.*) formed by the action of phosphorus oxychloride on (III; R = H, R′ = OH) (Blount and Plant, *J.*, 1937, 376).

The nature of the compound (B) which Barnes *et al.* described as a primary amine soluble in aqueous sodium hydroxide was not immediately clear but its conversion into (C), *i.e.*, (III; R = Br, R′ = OH), with alkalis suggested that it was the lactam (IV; R = Br) analogous to (IV; R = H) obtained by Witkop (*J. Amer. Chem. Soc.*, 1950, **72**, 1429) from 1 : 2 : 3 : 4-tetrahydrocarbazolyl hydroperoxide. Accordingly the lactam (IV; R = Br) was prepared by ozonolysis of 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole and,

* Part IV, *J.*, 1952, 4946.

although this compound, which formed an acetyl derivative, gave a negative diazo-test for a primary amine, it readily dissolved in warm dilute hydrochloric acid and the solution then gave a positive diazo-test. The compound (B), therefore, is regarded as the lactam (IV; R = Br).

The properties given by Barnes *et al.* for compounds (A), (B), and (C) and for the compounds described in the present work are summarised in the Table. In view of the agreement between the two series we consider that (A), (B), and (C) have the structures (II), (IV; R = Br), and (III; R = Br, R′ = OH) respectively, and that their formation has no bearing on the mechanism of the Fischer indole synthesis.

Compounds of Barnes *et al.* (*loc. cit.*)	Compounds described in present paper
(A) $C_{12}H_{10}O_2NBr$, m. p. 146° (deflagration)	(II) 8-Bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl hydroperoxide, $C_{12}H_{12}O_2NBr$, m. p. 146—150° (vigorous decomp.)
(C) $C_{12}H_8ONBr$, m. p. 253°; semipicrate, m. p. 223—224°	(III; R = Br, R′ = OH) 8-Bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline, $C_{12}H_{10}ONBr$, m. p. 246° (decomp.); semipicrate, m. p. 224°
Amphoteric compound, $C_{12}H_{11}ON$, m. p. 341°, from (C)	(III; R = H, R′ = OH) 4-Hydroxy-2 : 3-*cyclo*pentenoquinoline, $C_{12}H_{11}ON$, m. p. *ca.* 330° (decomp.)
Base, $C_{12}H_{11}N$, m. p. 60°, from (C); picrate, m. p. 190°	(III; R = R′ = H) 2 : 3-*cyclo*Pentenoquinoline, $C_{12}H_{11}N$, m. p. 60—61°; picrate, m. p. 215° (decomp.)
(B) $C_{12}H_{10}O_2NBr$, m. p. 166°; acetyl derivative, m. p. 124°	(IV; R = Br) Lactam of δ-(2-amino-3-bromobenzoyl)valeric acid, $C_{12}H_{12}O_2NBr$, m. p. 164—165°; acetyl deriv., m. p. 126°

Experimental

For various m. p. see the Table.

[With T. Donavanik] *8-Bromo-1 : 2 : 3 : 4-tetrahydro-11-carbazolyl Hydroperoxide* (I).—8-Bromo-1 : 2 : 3 : 4-tetrahydrocarbazole, prepared by the method of Barnes *et al.* (*loc. cit.*), was purified by distillation. On being kept, a solution of this compound (2 g.) in a mixture of benzene (10 ml.) and light petroleum (50 ml.) slowly deposited the *hydroperoxide* (0·5 g.) which, on recrystallisation from ethyl acetate, formed colourless tablets (Found: C, 51·5; H, 4·2; N, 4·9; Br, 27·6. $C_{12}H_{12}O_2NBr$ requires C, 51·1; H, 4·3; N, 5·0; Br, 28·4%).

8-Bromo-4-hydroxy-2 : 3-cyclopentenoquinoline (III; R = Br, R′ = OH).—A solution of the aforementioned hydroperoxide (1 g.) in methanol (15 ml.) was added to 2N-sodium hydroxide (30 ml.) at room temperature and 24 hr. later the mixture was neutralised with acetic acid. Thus precipitated, *8-bromo-4-hydroxy-2 : 3-cyclopentenoquinoline* was purified from benzene and obtained in colourless needles (Found: C, 54·4; H, 4·1; N, 5·2. $C_{12}H_{10}ONBr$ requires C, 54·6; H, 3·8; N, 5·3%). This amphoteric compound formed a picrate which separated from alcohol in yellow needles.

A solution of the bromo-quinoline (0·25 g.) in 1% methanolic potassium hydroxide (10 ml.) containing Raney nickel (1·0 g.) was agitated in hydrogen for 10 min., filtered, and evaporated. A solution of the residue in water (4 ml.) was neutralised with acetic acid, giving 4-hydroxy-2 : 3-*cyclo*pentenoquinoline, which on purification from alcohol had m. p. 328—330° (decomp.), identified by comparison with an authentic specimen (Part II, *loc. cit.*) and by preparation of the methyl derivative, m. p. and mixed m. p. 218—219°.

4-Chloro-2 : 3-cyclopentenoquinoline.—When the initial reaction between 4-hydroxy-2 : 3-*cyclo*pentenoquinoline (1·6 g.) and phosphoryl chloride (7 ml.) had somewhat subsided the mixture was heated on the steam-bath for 2 hr. and evaporated in a vacuum. A filtered solution of the residue in water (10 ml.) was basified with aqueous ammonia, giving 4-chloro-2 : 3-*cyclo*pentenoquinoline (1·5 g.) which was purified by crystallisation from light petroleum and then by sublimation at 0·01 mm. and obtained in magnificent lustrous rhombs, m. p. 73° (Found: C, 71·0; H, 5·0; N, 6·6; Cl, 17·3. Calc. for $C_{12}H_{10}NCl$: C, 70·8; H, 4·9; N, 6·9; Cl, 17·4%) (cf. Blount and Plant, *loc. cit.*, who give m. p. 70°). The *picrate* separated from alcohol in yellow rods, m. p. 180—181° (Found: C, 49·7; H, 3·3; N, 12·7. $C_{18}H_{13}O_7N_4Cl$ requires C, 49·9; H, 3·0; N, 12·9%).

2 : 3-cyclopentenoquinoline.—(*a*) A solution of 4-chloro-2 : 3-*cyclo*pentenoquinoline (0·5 g.) in 2% methanolic potassium hydroxide (20 ml.) containing palladised calcium carbonate (0·5 g.;

2% of palladium) was agitated in hydrogen for 1½ hr. (1 mol. of hydrogen absorbed). On the addition of a little water to the residue left on evaporation of the filtered solution in a vacuum 2 : 3-*cyclo*pentenoquinoline separated as an oil (0·37 g.) which solidified and was purified by sublimation in a vacuum, forming colourless plates, m. p. 60—61° (Found: C, 85·3; H, 6·5; N, 8·1. Calc. for $C_{12}H_{11}N$: C, 85·2; H, 6·5; N, 8·3%). Borsche (*loc. cit.*) gives m. p. 59—60°. The *picrate* separated from alcohol in yellow needles (Found: N, 13·7. $C_{18}H_{14}O_7N_4$ requires N, 14·1%).

(*b*) A mixture of 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline (0·2 g.) and palladised charcoal (0·3 g.; 3% of palladium) was kept in a U-tube in a stream of hydrogen at 280—300° for 2 hr. The sublimate which had collected in the exit limb of the tube was dissolved in a little water, and the solution basified with 2N-sodium hydroxide, giving 2 : 3-*cyclo*pentenoquinoline, m. p. 60—61° after purification as in (*a*). On being rendered faintly acid with acetic acid the alkaline liquor gave 4-hydroxy-2 : 3-*cyclo*pentenoquinoline, m. p. 329—330° (decomp.).

Lactam of δ-(2-Amino-3-bromobenzoyl)valeric Acid.—A stream of ozone and oxygen was led into a solution of 8-bromo-1 : 2 : 3 : 4-tetrahydrocarbazole (1·2 g.) in methanol (20 ml.) at −50° for 1 hr. Triturated with ether, the gum left on evaporation of the solution solidified and on crystallisation from benzene or ethyl acetate gave the *lactam* in colourless needles (0·65 g.) (Found: C, 50·8; H, 4·2; N, 4·7. $C_{12}H_{12}O_2NBr$ requires C, 51·1; H, 4·3; N, 5·0%). With 2N-sodium hydroxide the lactam was smoothly converted into 8-bromo-4-hydroxy-2 : 3-*cyclo*pentenoquinoline, and on acetylation with acetic anhydride and pyridine gave an acetyl derivative, forming rosettes of needles from light petroleum.

UNIVERSITY OF LIVERPOOL. [*Received, April 2nd,* 1953.]

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496. *The Action of Grignard Reagents on Anhydro-sugars of Ethylene Oxide Type. Part II.* The Behaviour of 4 : 6-Benzylidene 2 : 3-Anhydro-α-methyl-D-alloside towards Ethyl- and Phenyl-magnesium halides.*

By G. N. RICHARDS and L. F. WIGGINS.

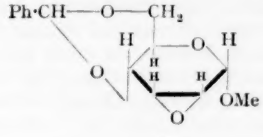
When 4 : 6-benzylidene 2 : 3-anhydro-β-methyl-D-allopyranoside is treated with methylmagnesium iodide 4 : 6-benzylidene 3-deoxy-3-iodo-α-methyl-D-glucopyranoside is the only product isolable (see Part I). With ethylmagnesium bromide or iodide the anhydro-sugar furnishes the corresponding 2-bromo- or 2-iodo-altrosides and no glucose isomer is obtained. The structure of the 2-bromo-2-deoxyaltroside is proved by its conversion into the known 2-bromo-2-deoxy-α-methyl-D-altroside and that of the 2-deoxy-2-iodoaltroside by its transformation into the crystalline 2-deoxy-α-methyl-D-alloside which is also obtained from the 2-bromo-2-deoxyaltroside. With phenylmagnesium bromide also, the 2 : 3-anhydroalloside yields 4 : 6-benzylidene 2-bromo-2-deoxy-α-methylaltroside but with zinc methyl iodide 4 : 6-benzylidene 3-deoxy-3-iodo-α-methyl-D-glucoside is obtained.

IN Part I* it was shown that 4 : 6-benzylidene 2 : 3-anhydro-α-methyl-D-allopyranoside (I) and methylmagnesium iodide yield 4 : 6-benzylidene 3-deoxy-3-iodo-α-methyl-D-glucopyranoside (II; R = I) only, the structure of which was proved by conversion into the known 4 : 6-benzylidene 3-deoxy-2-methyl-α-methyl-D-glucoside. The halogenoglucoside obtained from the anhydro-sugar arose from the cleavage of the oxide ring and the addition of the halide ion derived from the Grignard reagent and the authors suggested a mechanism for the reaction. According to the accepted ideas on the cleavage of αβ-anhydro-sugars by ionic reagents which have been summarized by Peat (*Adv. Carbohydrate Chem.*, 1946, **2**, 37), it would have been expected that both 4 : 6-benzylidene 2-deoxy-2-halogeno-α-methylaltroside and the corresponding 3-deoxy-3-halogenoglucoside would have been produced. However, only the latter could be isolated.

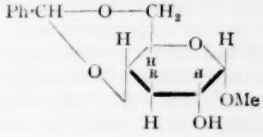
* Part I, *J.*, 1950, 2356.

The opening of oxide rings by neutral reagents is related to the present work and in this field the anhydroalloside has been treated with lithium aluminium hydride (Prins, *J. Amer. Chem. Soc.*, 1948, **70**, 3956) and with Raney nickel in an atmosphere of hydrogen (Prins, *Helv. Chim. Acta*, 1946, **29**, 1). The only product isolated from the first reaction was 4 : 6-benzylidene 2-deoxy-α-methylalloside, while in the second reaction the anhydroalloside was almost entirely converted into 3-deoxy-α-methylglucoside. This reversal of the direction of scission may be compared with the behaviour of the anhydroalloside towards methyl- and ethyl-magnesium iodides and serves further to emphasize the danger of attempting to predict the direction of scission of a given ethylene oxide ring by a given type of reagent.

In the present work the reaction of 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside (I) with ethylmagnesium iodide and bromide and with phenylmagnesium bromide has been examined. When the alloside (I) was treated with ethylmagnesium iodide in tetrahydropyran solution, only one of the isomeric 4 : 6-benzylidene deoxyiodo-α-methylhexosides was isolated (50% of the theoretical yield). This must be either 4 : 6-benzylidene 3-deoxy-3-iodo-α-methyl-D-glucoside (II; R = I) or 4 : 6-benzylidene 2-deoxy-2-iodo-α-methylaltroside (III; R = I), and it would be expected that the action of sodium methoxide on the deoxyiodohexoside would furnish the original alloside (I). This transformation was also accomplished when an attempt was made to methylate the 4 : 6-benzylidene deoxyiodo-α-methylhexoside under anhydrous conditions. This eliminates structures other than (II; R = I) or (III; R = I) for the deoxyiodohexoside. Since the compound possessed physical constants different from those of the known (II; R = I) it must be the isomeric altroside (III; R = I). This was verified by its transformation into crystalline 2-deoxy-α-methyl-D-allopyranoside (IV; R = H) by treatment with Raney nickel, according to the procedure described by Bougault, Cattelain, and Chabier (*Bull. Soc. chim.*, 1940, **7**, 781) for reductive desulphurization of thio-compounds. This compound was evidently identical with the amorphous 2-deoxy-α-methylalloside which Jeanloz, Prins, and Reichstein (*Helv. Chim. Acta*, 1946, **29**, 371) prepared by the reductive desulphurization of 4 : 6-benzylidene 2-deoxy-2-methylthio-α-methylaltroside (III; R = SMe). Nevertheless, an independent synthesis is described later.



(I)



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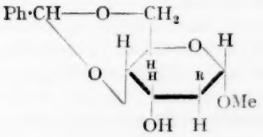

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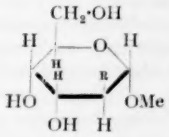

(IV)

When the reaction of the alloside (I) with ethylmagnesium bromide was studied, it was found that the only product isolated was an altroside derivative, namely, 4 : 6-benzylidene 2-bromo-2-deoxy-α-methyl-D-altropyranoside (III; R = Br), the structure of which was demonstrated by hydrolysis with oxalic acid in aqueous acetone; the benzylidene residue was removed and a crystalline product was obtained which rapidly consumed one mol. of lead tetra-acetate and was identical with the 2-bromo-2-deoxy-α-methylaltroside (IV; R = Br) of Newth, Overend, and Wiggins (*J.*, 1947, 10). Furthermore, alkaline hydrolysis of the 4 : 6-benzylidene 2-bromo-2-deoxy-α-methylaltroside (III; R = Br) afforded 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside (I). Hence the representation of the product of the reaction of ethylmagnesium bromide with the alloside (I) as (III; R = Br) must be correct.

When this compound was treated with Raney nickel in boiling ethyl alcohol, both the benzylidene and the bromine residue were removed and a deoxyhexoside was isolated, which, from the mode of synthesis must be 2-deoxy-α-methylalloside. This was identical with the compound derived from the product of the action of ethylmagnesium iodide on the alloside (I) and hence provides proof of the structure of that compound.

4 : 6-Benzylidene 2 : 3-anhydro-α-methylalloside (I) and phenylmagnesium bromide gave the same 2-bromo-2-deoxyaltroside (III; R = Br) as was obtained with ethylmagnesium bromide, although the product was more complex and the yield of altroside only 38%.

It is therefore evident that when the ethylene oxide ring of 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside is cleaved by ethylmagnesium bromide or iodide or by phenylmagnesium bromide, the only substance isolated was the 2-deoxy-2-halogenoaltroside, whereas methylmagnesium iodide gave, as main product, the alternative isomer, namely, a 3-deoxy-3-iodoglucoside. It is remarkable that replacement of methyl by ethyl in the Grignard reagent should have changed the direction of fission, but, since phenyl has the same effect as ethyl, the result may possibly be due to the size of the group in the Grignard complex. It was of interest that when the anhydroalloside was treated with methylzinc iodide, a substance closely similar to the Grignard reagent yet containing the larger metal ion, the reaction was similar to that with methylmagnesium iodide.

Experimental

Reaction of 4 : 6-*Benzylidene* 2 : 3-*Anhydro-α-methyl-*D-*alloside with Ethylmagnesium Iodide.*—The Grignard reagent was prepared in the usual manner from ethyl iodide (1·62 g.; freshly distilled), magnesium turnings (0·25 g.), and dry tetrahydropyran (10 c.c.). To this was added, at room temperature, a solution of the alloside (2·5 g.) in warm tetrahydropyran (150 c.c.), at <20°. A heavy white granular precipitate was formed and the colour deepened to dark orange. On boiling, the precipitate dissolved and after 1 hr.' refluxing the colour faded and a very fine, white precipitate was deposited. After cooling to room temperature, ice was added, followed by dilute hydrochloric acid. The tetrahydropyran layer was immediately washed with sodium hydrogen carbonate and sodium thiosulphate solutions and with water, dried (Na_2SO_4), and evaporated to dryness. The residue was fractionated as described for a similar experiment with ethylmagnesium bromide (see below); 0·876 g. of starting material was recovered unchanged, together with well-formed cubic crystals of 4 : 6-*benzylidene* 2-*deoxy*-2-*iodo*-α-*methyl*-D-*altroside*, which on recrystallisation from ethyl alcohol had m. p. 105—106°, $[\alpha]_D^{20}$ +39·0° in $CHCl_3$ (*c*, 1·333) (1·681 g., 47%) (Found: C, 43·1; H, 4·4. $C_{14}H_{17}O_5I$ requires C, 42·8; H, 4·3%).

Acetylation of 4 : 6-*Benzylidene* 2-*Deoxy*-2-*iodo*-α-*methyl*-D-*altroside.*—The altroside (1·075 g.) when treated and acetic anhydride (2 c.c.) in pyridine (10 c.c.) at 30° (18 hr.) gave an amorphous solid (1·185 g.), isolated by means of chloroform. This was dissolved in ether–acetone, filtered, and again evaporated to dryness, giving 3-*acetyl* 4 : 6-*benzylidene* 2-*deoxy*-2-*iodo*-α-*methyl*-*altroside*, which after being dried at 50°/0·2 mm. showed $[\alpha]_D^{17}$ +12·8° in $CHCl_3$ (*c*, 1·56) (Found: C, 44·4; H, 4·5. $C_{16}H_{19}O_6I$ requires C, 44·2; H, 4·4%).

4 : 6-*Benzylidene* 3-*Toluene*-p-*sulphonyl* 2-*Deoxy*-2-*iodo*-α-*methyl*-D-*altroside.*—4 : 6-Benzylidene 2-deoxy-2-iodo-α-methylaltroside (0·150 g.) and toluene-*p*-sulphonyl chloride (0·2 g.) in pyridine (5 c.c.) at 30° (18 hr.) gave a syrupy product which solidified under water overnight. The 3-*toluene*-p-*sulphonate* (0·115 g.) was then collected, washed with water, and recrystallized from aqueous ethyl alcohol. It had m. p. 114·5—115° (decomp.), $[\alpha]_D^{18}$ −15·6° in $CHCl_3$ (*c*, 0·769) (Found: C, 45·6; H, 3·95. $C_{21}H_{23}O_7IS$ requires C, 46·1; H, 4·2%).

Reduction of 4 : 6-*Benzylidene* 2-*Deoxy*-2-*iodo*-α-*methylaltroside with Raney Nickel.*—To a solution of the altroside (0·43 g.) in ethyl alcohol (20 c.c.) was added barium carbonate (2 g.), followed by Raney nickel (*ca.* 7 g.; Mozingo, *J. Amer. Chem. Soc.*, 1943, **65**, 1013), suspended in the same solvent (*ca.* 10 c.c.). After the addition of water (7 c.c.) the mixture was warmed under reflux for 1½ hr., cooled, and filtered, the residual solids being washed several times with hot water. The combined filtrates were evaporated under reduced pressure and the residue was redissolved in water (5 c.c.), extracted several times with chloroform to remove unchanged starting material, and again evaporated to dryness. The residue was then extracted with ethyl acetate, filtered to remove barium iodide, and once more evaporated. The dried residue,

crystallized from ether–ethyl alcohol–light petroleum (b. p. 60—80°), had m. p. 91—93° alone or in admixture with 2-deoxy-α-methylalloside prepared from 4 : 6-benzylidene 2-bromo-2-deoxy-α-methylaltroside (see below). The yield was 0·158 g. (81%).

Alkaline Hydrolysis of 4 : 6-*Benzylidene* 2-*Deoxy*-2-*iodo*-α-*methylaltroside*.—A solution of the altroside (0·120 g.) in chloroform (1 c.c.) was treated with a solution of sodium (0·1 g.) in absolute methyl alcohol (5 c.c.) at 0°. The needle-shaped crystals formed (0·065 g., 80%) were removed by filtration and washed with ether; they had m. p. 199—200·5° alone or in admixture with authentic 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside.

Attempted Methylation of 4 : 6-*Benzylidene* 2-*Deoxy*-2-*iodo*-α-*methylaltroside*.—The altroside (1·209 g.) was heated under reflux with dry methyl iodide (10 g.) and dry silver oxide (*ca.* 5 g.). White needles began to separate after several hours and, after refluxing had continued overnight, the solution was filtered and the residual solids were washed several times with boiling chloroform. The combined filtrates were evaporated under reduced pressure. The colourless solid residue (0·811 g.), when recrystallized from ethyl alcohol, showed m. p. 199—200° alone or in admixture with authentic 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside.

Action of Ethylmagnesium Bromide on 4 : 6-*Benzylidene* 2 : 3-*Anhydro*-α-*methylalloside*.—To the Grignard reagent prepared from ethyl bromide (1·13 g.), magnesium turnings (0·249 g.), and dry tetrahydropyran (10 c.c.), at room temperature, was added slowly the alloside (2·453 g.) in warm tetrahydropyran (150 c.c.). A very fine colourless precipitate separated. After 2 hr.' refluxing, ice was added, followed by a slight excess of dilute hydrochloric acid. The ethereal layer was washed with sodium hydrogen carbonate solution and with water, dried (Na_2SO_4), and evaporated. The semi-solid residue was extracted with ethyl alcohol (100 c.c.) at room temperature. An insoluble portion (0·522 g.) had m. p. 196—199° and was of unchanged starting material. The alcoholic solution was evaporated and the crystalline residue fractionally recrystallized from ethyl alcohol–ether, giving a further 0·335 g. of unchanged starting material (total, 35%) together with 4 : 6-*benzylidene* 2-*bromo*-2-*deoxy*-α-*methylaltroside*, which crystallized from ethyl alcohol–ether as cubes m. p. 117·5—118·5°, $[\alpha]_D^{19}$ +58·0° in $CHCl_3$ (*c*, 2·478) (1·635 g., 51%) (Found: C, 48·7; H, 5·1. $C_{15}H_{17}O_5Br$ requires C, 48·7; H, 4·9%).

Treatment of 4 : 6-*Benzylidene* 2-*Bromo*-2-*deoxy*-α-*methylaltroside with Toluene*-p-*sulphonyl Chloride*.—The altroside (0·246 g.) was treated in dry pyridine (5 c.c.) with toluene-*p*-sulphonyl chloride (0·3 g.) at room temperature for 24 hr. The solution was then poured into water, giving a yellow solid. This was collected and washed with water. Recrystallized from ethyl alcohol, 4 : 6-*benzylidene* 2-*toluene*-p-*sulphonyl* 2-*bromo*-2-*deoxy*-α-*methylaltroside* formed needles (0·142 g.), m. p. 159·5—160°, $[\alpha]_D^{19}$ +36·9° in $CHCl_3$ (*c*, 2·770) (Found: C, 50·3; H, 4·3. $C_{21}H_{23}O_7BrS$ requires C, 50·5; H, 4·6%).

Hydrolysis of 4 : 6-*Benzylidene* 2-*Bromo*-2-*deoxy*-α-*methylaltroside with Oxalic Acid*.—To the altroside (0·406 g.) in acetone (22·5 c.c.) oxalic acid (0·75 g. of the dihydrate in 2·5 c.c. of water) was added. The solution was heated under reflux for 24 hr. and thereafter neutralized with barium carbonate. The barium salts were removed and washed with hot water, the combined filtrates being evaporated to dryness under reduced pressure. The residue was distilled with steam until the odour of benzaldehyde was no longer detected and then dissolved in water, and the solution washed several times with chloroform to remove any unchanged starting material, filtered, and evaporated to dryness. The residue, recrystallized from ethyl alcohol, formed cubes of 2-bromo-2-deoxy-α-methylaltroside, m. p. 152—153·5° alone or in admixture with an authentic specimen prepared by Newth, Overend, and Wiggins (*loc. cit.*).

Alkaline Hydrolysis of 4 : 6-*Benzylidene* 2-*Bromo*-2-*deoxy*-α-*methylaltroside*.—The altroside (46 mg.) was dissolved in ethyl alcohol (1·2 c.c.), and 5N-sodium hydroxide (0·1 c.c.) added at room temperature. A colourless solid separated and after being kept at room temperature for 3 hr. this was collected, washed with water, and dried under reduced pressure over phosphoric oxide. It (35 mg.) had m. p. 198—200° alone or in admixture with 4 : 6-benzylidene 2 : 3-anhydro-α-methylalloside.

Reduction of 4 : 6-*Benzylidene* 2-*Bromo*-2-*deoxy*-α-*methylaltroside with Raney Nickel*.—To a solution of the altroside (0·96 g.) in ethyl alcohol (40 c.c.) was added barium carbonate (4 g.) followed by Raney nickel (*ca.* 15 g.; cf. above) suspended in the same solvent (*ca.* 20 c.c.). Water (15 c.c.) was added and the mixture warmed under reflux for 1½ hr. Bromide ion was detected in the solution after a few minutes and the odour of toluene was noted. The cooled solution was filtered, the residual solid was washed with hot water, and the combined filtrates were evaporated under reduced pressure. The residue was dissolved in water (10 c.c.), extracted several times with chloroform, and again evaporated to dryness. When the syrupy residue was dried at 50° at 0·2 mm. over phosphoric oxide, crystallization was induced and was completed

by trituration with ether. Recrystallized from ether–ethyl alcohol–light petroleum, 2-deoxy-α-methylalloside (altroside) formed very hygroscopic cubes (0·412 g., 83%), m. p. 91—93° (rapid heating), $[\alpha]_D^{19}$ +144·0° in $CHCl_3$ (*c*, 0·376) (Found: C, 46·8; H, 7·75. Calc. for $C_7H_{14}O_5$: C, 47·2; H, 7·9%). Jeanloz, Prins, and Reichstein (*loc. cit.*) give $[\alpha]_D^{13}$ +143·1° ± 2° in $CHCl_3$ (*c*, 0·978).

Oxidation of 2-Bromo-2-deoxy-α-methylaltroside with Lead Tetra-acetate.—The bromoaltroside ($2·12 \times 10^{-4}$ mole) consumed the following amounts of lead tetra-acetate under conditions prescribed by Hockett and McClenahan (*J. Amer. Chem. Soc.*, 1939, **61**, 1667): 0·621 g.-atom of O (5 min.), 0·818 (10 min.), 0·953 (20 min.), 0·99 (30 min.), and 0·98 (60 min.).

Reaction of 4 : 6-Benzylidene 2 : 3-Anhydro-α-methylalloside with Phenylmagnesium Bromide.—To a solution of the Grignard reagent [from bromobenzene (1·64 g.) and magnesium turnings (0·25 g.) in tetrahydropyran (15 c.c.)], kept at <20°, was added the anhydroalloside (2·45 g.) in warm tetrahydropyran (150 c.c.). After 1 hr. heating, during which a fine colourless granular precipitate separated, the solution was allowed to cool to room temperature, and ice and a slight excess of 5N-hydrochloric acid were added. The ethereal layer was washed with sodium hydrogen carbonate solution and with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was fractionated as described for the reaction with ethylmagnesium bromide; unchanged starting material (0·96 g., 39·2%) was isolated, together with 4 : 6-benzylidene 2-bromo-2-deoxy-α-methylaltroside (1·299 g., 38·3%), m. p. 117—118·5° alone or in admixture with the compound obtained from the reaction with ethylmagnesium bromide. The mother-liquors yielded on evaporation a colourless syrup (0·898 g.) having a characteristic sweet odour. Distillation of this product occurred in two fractions: (i), b. p. 90—95° (bath-temp.)/0·04 mm., a colourless, mobile liquid (0·177 g.), n_D^{13} 1·4978, α ±0°, contained bromine but was not identified (Found: C, 65·8; H, 8·3%); (ii) b. p. at 145—150° (bath-temp.)/0·035 mm., a colourless, viscous liquid (0·104 g.), n_D^{19} 1·4930, $[\alpha]_D^{22}$ +11·7° in $CHCl_3$ (*c*, 1·88), contained bromine, but was not identified (Found: C, 65·85; H, 9·1%). The remainder of the product decomposed without further distillation below 165° at the same pressure.

Treatment of 4 : 6-Benzylidene 2 : 3-Anhydro-α-methylalloside with Methylzinc Iodide.—The reagent was prepared essentially by Blaise's method (*Bull. Soc. chim.*, 1911, **4**, 9). The final reaction mixture was then made faintly acid with dilute hydrochloric acid, and the toluene layer separated, washed with sodium hydrogen carbonate and sodium thiosulphate solutions and with water, dried (Na_2SO_4), and evaporated under reduced pressure. The colourless solid residue, recrystallized from chloroform–light petroleum (b. p. 60—80°), had m. p. 194—195° alone or in admixture with 4 : 6-benzylidene 3-deoxy-3-iodo-α-methylglucoside (yield, 2·0 g., 45%).

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497. *Dielectric Dispersion in Sulphuric Acid.*

By J. C. D. Brand, (the late) J. C. James, and A. Rutherford.

The complex dielectric constant of anhydrous sulphuric acid has been measured at six frequencies between 100 and 3000 Mc. The results are compatible with a small distribution of relaxation times and are analysed by the semi-empirical equation (Cole and Cole, *J. Chem. Phys.*, 1941, **9**, 341)

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = \varepsilon_\alpha + (\varepsilon_0 - \varepsilon_\alpha)/\{1 + (i\omega\tau_0)^{1-\alpha'}\} \quad . \quad . \quad . \quad (1)$$

wherein ε_0 and ε_α are, respectively, the low- and the high-frequency limiting dielectric constants, τ_0 is the most probable relaxation time, and α' is a parameter governing the spread of relaxation times. The parameters which best fit the experimental results are, at 20° : $\varepsilon_\alpha = 5$ (assumed), $\varepsilon_0 = 110$, $\tau_0 = 4{\cdot}8 \times 10^{-10}$ sec., and $\alpha' = 0{\cdot}085$. The high electrolytic conductance introduces considerable experimental difficulties, and the extrapolation of ε_0 is uncertain to several units. The significance of the dielectric constant is discussed in relation to the thermodynamic properties of solutions in sulphuric acid.

It is well known that electrolyte solutions in sulphuric acid are thermodynamically nearly ideal, even at very high ionic strengths. This property was first appreciated by Hammett and Deyrup who suggested, as the most rational explanation, that the dielectric constant of the acid must be " extremely high " (Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940). More recently it has been found that solutions of non-electrolytes in sulphuric acid are, on the whole, *less* nearly ideal than the electrolytic solutions, and opinion has veered towards the view that the dielectric constant is so very high that electrostatic forces between ions are negligible. On this hypothesis (Gillespie, Hughes, and Ingold, *J.*, 1950, 2473) the need to consider electrolytes and non-electrolytes as separate classes disappears and only solvation, or other equilibria, are considered to cause the small but measurable defects from ideality.

Walden, in 1903 (*Z. physikal. Chem.*, **46**, 182), reported that the dielectric constant of " concentrated " sulphuric acid was higher than that of water. However, this conclusion involved the tacit assumption that the dielectric was lossless, a condition very far indeed from being fulfilled. Assuming that Walden used 96% acid we can estimate from our results that the loss tangent was not lower than 10 at the operating frequency (417 Mc., 72 cm.) and that the dielectric constant was probably only 30—40, considerably less than in water; but no optical method would give an accurate value of the dielectric constant of a liquid with so high a loss. By using *anhydrous* sulphuric acid, which has a much lower electrolytic conductance, it is possible to make reasonably accurate measurements at high frequencies, and hence to extrapolate the limiting low-frequency dielectric constant within a few units; the uncertainty of the extrapolation is still due mainly to the residual d.c. conductance of the anhydrous acid.

The theory of an ideal polar dielectric in an alternating field was developed by Debye (" Polar Molecules," Chemical Catalogue Co., New York, 1929). Except for the assumption of a single relaxation time, the basic equations (2) are independent of the dielectric model.

$$\left.\begin{aligned} \varepsilon = \varepsilon_1 - i\varepsilon_2 &= \varepsilon_\alpha + (\varepsilon_0 - \varepsilon_\alpha)/(1 + i\omega\tau) \\ \text{where} \quad \varepsilon_1 &= (\beta^2 - \alpha^2)/\beta_0{}^2 \\ \text{and} \quad \varepsilon_2{}^{\mathrm{T}} &= 2\alpha\beta/\beta_0{}^2 = \varepsilon_2 + \varepsilon_2{}^{\mathrm{C}} = \varepsilon_2 + 4\pi\kappa/\omega \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

In eqn. (2), ε_1 is the dielectric constant (variable with frequency) and $\varepsilon_2{}^{\mathrm{T}}$ is the total dielectric loss factor, ε_2 and $\varepsilon_2{}^{\mathrm{C}}$ being the loss factors relating to dipole orientation and d.c. conductance, respectively, ε_0 and ε_α are the limiting low- and high-frequency dielectric constants, and ε is the complex dielectric constant at the angular frequency ω, τ is the relaxation time corresponding to the wave-length $\lambda_m = 2\pi c\tau$ at which ε_2 is a maximum, and κ is the d.c. conductance in e.s.u. α and β are, respectively, the attenuation constant and the phase constant of classical electromagnetic theory, β_0 being the phase constant for

propagation *in vacuo*; α, β, and β_0, and hence ε_1 and ε_2^T, are experimentally measurable quantities. Although the assumption of a single relaxation time is verifiable for some dielectrics, real systems are often better described by the modified, semi-empirical expression (1) (see Summary), where the symbols have the same meaning except that the relaxation process is specified by τ_0 and α' in place of τ.

Measurements with sulphuric acid were made in the decimetre and metre wave-bands at a single temperature (20°). Different experimental methods were used in the two regions, but the general principle was to determine β and α in a coaxial wave-guide from the phase and power of the wave transmitted through a column of the dielectric. The mode in the guide was purely transverse. The derived values of ε_1 and ε_2 were more consistent with eqn. (1) than with the Debye equations, although the spread of relaxation times was quite small. ε_0, τ_0, and α' were obtained as parameters, the maximum loss due to dipole reorientation being at 330 ± 30 Mc ($\lambda_m = 90$ cm.).

Experimental

Measurements at 100—300 Mc.—The generator was a conventional variable-frequency oscillator incorporating a miniature triode (Mullard EC53), a tuned crystal detector being used to monitor the relative power levels. The rectified current from the crystal is proportional to (voltage)^2, and hence is proportional to power if the voltage is developed across a constant impedance. The tuning of the detector by a variable reactance (an adjustable short-circuited length of concentric line at 300 Mc and a lumped circuit at 250—100 Mc) discriminates against the rectification of harmonics.

The " square-law " characteristic of the crystals was tested by measurements on the standing-wave in a slotted guide with a short-circuit termination (Birks, *Proc. Phys. Soc.*, 1948, **60**, 282). The voltage distribution on the line is

$$V^2 = V_0^2 \sin^2 (2\pi x/\lambda)$$

where V_0 is the maximum voltage, and V is the voltage at a distance x from the minimum. If the " square-law " characteristic holds accurately the crystal current, i, must be proportional to $\sin^2 (2\pi x/\lambda)$, and this was verified with a probable error of less than 1% over a complete quarter wave-length, *i.e.*, for the voltage range zero to V_0. The proportionality found in this experiment also proves that harmonics present in the output of the generator are not rectified by the crystal. In actual measurements the crystal current was always <1 μa, and was measured by a galvanometer previously calibrated against a standard microammeter.

Dielectric Cells.—These were telescopic sections of coaxial wave-guide, and two such cells were employed. In one, the outer conductor (diam. 4·43 cm.) was of copper and the inner conductor (1·28 cm.) of brass, the surfaces being gold-plated (0·004 cm.); the length was 30 cm. The inner conductor was held centrally by a " Polythene " disc which also provided a liquid-tight seal. The telescopic section of the cell, which did not come into contact with sulphuric acid and was unplated, was in sliding contact with the gold-plated surfaces and was moved by hand. Connections were made by flexible coaxial cable (Uniradio 21) through G.E.C. coaxial sockets. Control measurements with aqueous electrolyte solutions showed that there was no interference from subsidiary modes. The second cell was similar, but was constructed of stainless steel which is not attacked by sulphuric acid. The outer and inner conductor diameters were, respectively, 3·81 and 1·27 cm. The expectation that this cell might prove appreciably resistive to high-frequency current, owing to the surface film of oxide, was not realised and the results with the two cells were indistinguishable. Preliminary measurements were made with a gold-plated cell 14 cm. long; this was designed in the expectation of a much higher dielectric constant and in practice did not provide a sufficiently long " optical path " of dielectric.

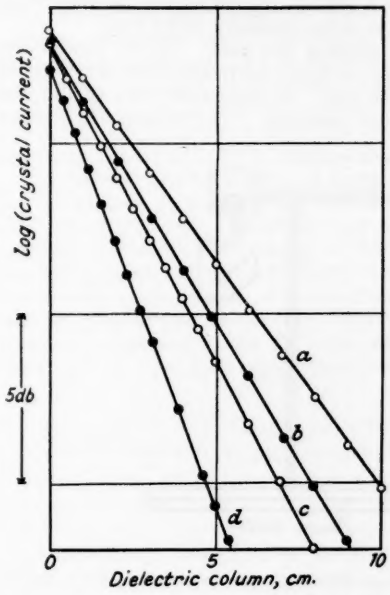
Measurement of Attenuation Coefficient.—The measurement of α (cf. Turner, *J. Inst. Elect. Eng.*, 1946, IIIA, **93**, 1474) is the same in principle as the measurement of percentage transmission at optical and infra-red frequencies with a cell of variable thickness. Power is the analogue of intensity, the relation between transmitted power, P, and the dielectric path, l, being

$$P = P_0 \exp(-2\alpha l) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

α is obtained by plotting the logarithm of the crystal current ($i \propto P$) against the length of the dielectric column (Table 1 and Fig. 1).

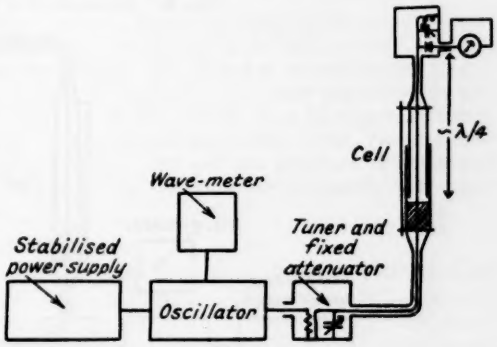
The arrangement of the apparatus is shown in Fig. 2. At radio-frequencies certain conditions need to be fulfilled which do not have an optical analogy. First, on the side of the crystal detector the electrical length from the surface of the dielectric to the short circuit must remain constant, or eqn. (3) is not fulfilled : * a constant length was maintained by raising the telescopic section of the cell after each addition of sulphuric acid. Secondly, the power level sent from the generator into the cell must remain constant as the dielectric path changes. This is achieved if the *initial* length of the dielectric column is such that at least 90% of the incident power is absorbed by the column, because the power reflected to the generator from the upper surface of the dielectric is then negligible and additions to the dielectric column do not change

FIG. 1. *Power attenuation in* H_2SO_4



	λ, cm.	α, decibels cm.$^{-1}$	κ_{30}, ω^{-1} cm.$^{-1}$
Curve *a*	304	1·35	0·00866
,, *b*	198	1·64	0·00857
,, *c*	157	1·86	0·00860
,, *d*	108	2·69	0·00875

FIG. 2. *Measurement of attenuation coefficient.*



the impedance of the load as seen from the generator. The generator was tuned to the load by a small variable condenser.

The sulphuric acid was added to the cell from a burette, the height of the liquid in the cell being calculated from the volume and the cross-sectional area. The acid in the burette was protected by phosphoric oxide guard tubes, and a stream of dry nitrogen was passed over the surface of the liquid in the cell to minimise absorption of moisture. The d.c. conductance of the acid in the cell was measured at the conclusion of the experiment.

Measurement of the Phase Constant.—The phase constant $\beta = 2\pi/\lambda_d$ was determined by measuring λ_d, the wave-length of the radiation in the dielectric. An interferometric method was employed (Fig. 3). Power from the generator was sent partly through the dielectric cell, and partly into a correctly-terminated slotted guide which was a reference source of radiation of varying phase at constant amplitude. The resultant power from the top of the dielectric cell and from a probe on a travelling detector in the slotted guide was monitored by a crystal. When the wave through the dielectric is out-of-phase with the wave from the slotted line the power registered at the crystal termination is a minimum. In operation, the depth of sulphuric acid

* Because α is defined in terms of voltage, $E = E_0 \exp(-\alpha l)$; power is proportional to E^2 only if the impedance is constant.

in the cell was increased stepwise and the position of the travelling probe which minimised the crystal current found after each addition. The wave-length in the dielectric was given by :

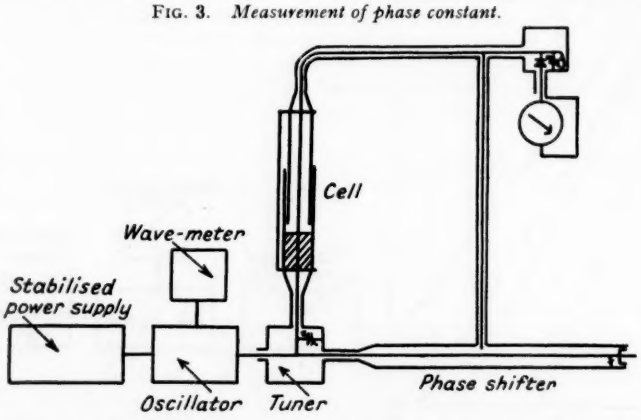
$$\frac{\lambda_d}{\lambda_0} = \frac{\beta_0}{\beta_d} = \frac{\text{Added height of dielectric column}}{\text{Probe movement along slotted line}}$$

λ_0 being the free-space wave-length (Table 1).

As in the measurement of α, the initial path of the dielectric must be sufficiently attenuative effectively to isolate the two halves of the apparatus. The sensitivity of the apparatus is optimal if the power load in the two arms is equal, so that the power received by the crystal is zero when the waves are exactly out of phase; this was achieved by adjusting the depth of the probe in the slotted guide. The telescopic cell was extended after each addition of sulphuric acid. The free-space wave-length was measured on a section of short-circuited line, very loosely coupled to the generator; tests showed no pulling of the oscillator under load.

Measurements at 1120 *and* 3000 Mc.—A reflection method was used. At the face of the dielectric sample partial reflection occurs, and interference between the incident and the reflected waves sets up a standing-wave in the line above the dielectric. An attenuator (20—50 db.) was inserted to prevent the reflected wave from reaching the oscillator. The voltage distribution

FIG. 3. *Measurement of phase constant.*



along the standing-wave and the position of the voltage minima were determined by a crystal probe in a travelling detector.

The calculation of ε_1 and $\varepsilon_2{}^T$ from the standing-wave pattern is straightforward if the dielectric column quantitatively absorbs the incident radiation. With sulphuric acid, which has a high loss at these frequencies, this condition is easily satisfied, and it can then be shown (Willis Jackson, *Trans. Faraday Soc.*, 1946, **42**, *A*, 91) that the voltage–standing-wave ratio, $s = V_{max.}/V_{min.}$, is equal to $|\varepsilon|^{\frac{1}{2}}$, where $|\varepsilon|$ is the modulus of the complex dielectric constant,

$$\varepsilon = \varepsilon_1 - i\varepsilon_2{}^T = |\varepsilon| \exp(-i\delta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

s was evaluated from the probe positions at which the power level was $2V_{min.}$ by the equation $s^2 = 1 + \text{cosec}^2 \beta_0 x_0$, $2x_0$ being the distance between points on each side of the minimum at which $i/i_{min.} = (V/V_{min.})^2 = 2$ (Birks, *loc. cit.*). The phase angle δ (eqn. 4) was calculated from the distance x of the first voltage minimum from the surface of the dielectric by the expression $\delta \simeq 2 \tan^{-1} [(s - 1/s) \tan \beta_0 x]$.

Also, from eqn. (4), $\delta = \tan^{-1} (\varepsilon_2{}^T/\varepsilon_1)$. Hence ε_1 and $\varepsilon_2{}^T$ can be calculated from the measurements of s and x. ε_2 is obtained from $\varepsilon_2{}^T$ by subtracting the electrolytic conductance, $4\pi\kappa/\omega$.

Owing to the meniscus on the liquid surface, the value of x is unsharp. x was measured from the voltage minimum to the liquid surface at a standard distance (1 mm.) from the centre conductor. Control experiments with aqueous electrolyte solutions showed that the values of $\tan \delta$ calculated from the measurement of x were uncertain to 20%. The derived results for ε_1 and ε_2 (Table 1) must be regarded as qualitative.

At 3000 Mc a standard reflex klyston was used, very loosely coupled to the wave-guide system through a coaxial cable. The coaxial wave-guide, which was silver-and-rhodium-plated, had inner and outer conductor diameters of 0·775 and 2·225 cm. and a slot length of 16 cm. The

cells had the same cross-section and were of various lengths up to 10 cm. The centre conductor of the slotted line was held by a " Polythene " plug at the upper end and by the central pillar of the dielectric cell at the foot. The movement of the detector carriage was measured (to 0·002 cm.) by a micrometer dial gauge, and the free-space wave-length was observed between successive voltage minima in the slotted guide, a short-circuit termination being used. At 1120 Mc the oscillator was a 446 tube with concentric line tuning; the slotted line was the same element used in measurement of the phase constant, and the position of the detector carriage was read on a 0·1-mm. vernier scale.

Alternation Coefficient of Aqueous Sulphuric Acid at 30—100 Mc.—These measurements were undertaken to determine whether the electrolytic conductance of sulphuric acid is variable with frequency. The cells described on p. 2448 were used. At low frequencies it was advantageous to have a coaxial line connection, approx. $\lambda/4$, from the surface of the dielectric to the crystal detector; a lumped circuit sufficed for the line termination. The components of the lumped circuit were varied according to the measuring frequency. The free-space wave-length at 60—100 Mc was measured on a short-circuited line. At 30 Mc (experiments by J. Hossack) the wave-length was measured by a heterodyne wave-meter calibrated against a crystal oscillator. The results for the aqueous acids (96—99·5% H_2SO_4) and for a solution of potassium nitrate in sulphuric acid are in Table 3.

Conductivity Measurements and Temperature Control.—The composition of the sulphuric acid was determined by conductivity measurement. The anhydrous acids were initially 100·01—100·04% H_2SO_4; some moisture was absorbed during the dielectric measurements, corresponding to a composition change of 0·005—0·01% of H_2SO_4, but the error introduced in this way is negligible. The conductivity was measured at 20° ± 0·01° in a U-shaped cell with bright platinum electrodes, with a screened a.c. bridge (James and Knox, *Trans. Faraday Soc.*, 1950, **46**, 254) at frequencies from 1000 to 3000 c. sec.$^{-1}$. The cell was calibrated by means of Jones and Bradshaw's data for potassium chloride. The dielectric measurements were made at 20° ± 1° in a constant-temperature room.

Discussion

High-frequency radiation is attenuated in sulphuric acid by two independent mechanisms, dipole reorientation and electrolytic conductance. The reorientation process is a classical model of the rotational absorption spectrum, and is necessarily accompanied by dispersion of the dielectric constant. The rotational absorption in a pure polar liquid is a weak, very broad band covering about two decades of frequency, the intensity of absorption being described by the dielectric loss factor (ε_2) which is proportional to the power attenuation per wave-length. The conductance also causes power attenuation, expressed in the same units by $\varepsilon_2^C = 4\pi\kappa/\omega$, and to obtain ε_2 the term ε_2^C must be subtracted from the total loss factor ($\varepsilon_2^T = \varepsilon_2 + \varepsilon_2^C$) measured experimentally. κ is assumed not to vary with frequency, and this assumption is discussed later.

The relation between dispersion and dipolar absorption is brought out by plotting ε_1 and ε_2 on perpendicular axes, each point referring to one frequency (Fig. 4). If there is a single relaxation time the Debye equations (2) are valid, and the theoretical locus of the points is a semicircle on the abscissa with intercepts ε_0 and ε_α; in this case the dispersion ($\varepsilon_0 - \varepsilon_\alpha$) equals twice the maximum value of ε_2. Real dielectrics are often better described by eqn. (1), which is an empirical modification of eqn. (2) and introduces a new parameter α' to define the distribution of relaxation times (Cole and Cole, *J. Chem. Phys.*, 1941, **9**, 341). Other forms of distribution function have been proposed but they are indistinguishable experimentally, particularly when the distribution of times is small (Kauzmann, *Review Mod. Phys.*, 1942, **14**, 12). With a distribution of relaxation times the (ε_1, ε_2) points fall on a circular arc with intercepts ε_0 and ε_α, the centre of the circle lying below the horizontal axis. The axis is now a chord and not a diameter of the circle and the dispersion, enclosed by the two intersections with the axis, is greater than twice the maximum value of ε_2. The results for sulphuric acid are more consistent with the Cole–Cole expression than with the Debye equation although, owing to the correction for electrolytic conductance, the experimental uncertainty is rather high. The required distribution of relaxation times is small.

The parameters α' and τ_0 are evaluated by the equation

$$(\varepsilon_1 - \varepsilon_\alpha)/\varepsilon_2 - \tan(\alpha'\pi/2) = (\lambda_m/\lambda)^{1-\alpha'};\ \lambda_m = 2\pi c\tau_0$$

obtained by rearrangement of eqn. (1). The two sides of this expression are plotted logarithmically in Fig. 5. α' determines the gradient but also contributes a small term to the ordinate, and the best value is found by trial and error; λ_m, and hence τ_0, is then found from the intercept with log $[(\varepsilon_1 - \varepsilon_\infty)/\varepsilon_2 - \tan(\alpha'\pi/2)] = 0$. In this calculation we have assumed $\varepsilon_\infty = 5$, a value which seems to be typical of associated liquids, including water and the lower alcohols (Lane and Saxton, *Proc. Roy. Soc.*, 1952, *A*, **213**, 400, 473; Cole and Davidson, *J. Chem. Phys.*, 1952, **20**, 1389). The assumed value of ε_∞ is not critical because α' and τ_0 are mainly determined by the results at 1—3 m. where $\varepsilon_1 - \varepsilon_\infty$ is large, but the overall uncertainty, *e.g.*, in τ_0, must be estimated at not less than 10%. α' from Fig. 5 was used to construct the arc in Fig. 4. The parameters describing the dispersion are summarised in Table 2, and the calculated values of the attenuation coefficient and phase constant are given in Table 1. Table 1 is a better test of agreement than the graphical representation in Fig. 4 because the circular arc plot, where frequency does not appear explicitly, does not show whether the $(\varepsilon_1, \varepsilon_2)$ points are consistent with ω.

FIG. 4. *Complex dielectric constant of* H_2SO_4 (20°).

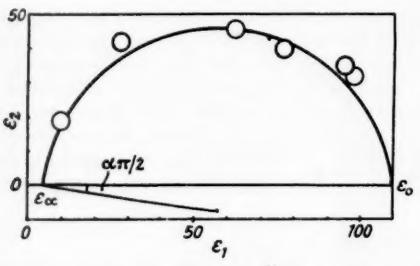


FIG. 5. *Evaluation of* α' *and* λ_m.

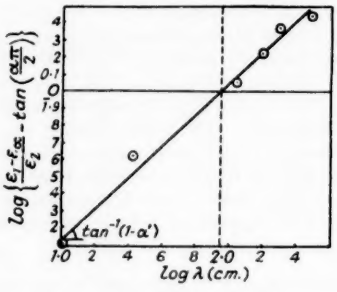


TABLE 1. *Dispersion and dielectric loss in anhydrous* H_2SO_4 (20°).

Frequency (Mc)	κ_{20} (ω^{-1} cm.$^{-1}$)	Attenuation coeff. (nepers cm.$^{-1}$) exp.	calc.	Phase constant (radians cm.$^{-1}$) exp.	calc.	$\varepsilon_\omega{}^T$	$\varepsilon_2{}^C$	ε_2	ε_1
99·0	0·00866	0·157	0·155	0·258	0·256	190	158	32	98
151·5	0·00875	0·190	0·199	0·364	0·357	139	104	35	95
191·5	0·0095	0·240	0·240	0·428	0·432	128	88	40	77
296	0·00870	0·310	0·314	0·553	0·564	102·4	56·5	45·6	62·5
1120	—	—	—	—	—	—	—	42	28
2940	—	—	—	—	—	—	—	19	10

Columns headed " calc. " are evaluated by eqn. (1) from the parameters in Table 2.

The molecular relaxation time for a spherical molecule rotating in a medium with an " inner " viscosity η is (Debye, *loc. cit.*) :

$$\tau_m = 3\pi\eta V/kT$$

η is usually identified with the macroscopic viscosity coefficient. The relation between the dielectric relaxation time (τ_0) and τ_m depends upon the assumption made for the local field in the dielectric. For the Mosotti field $\tau_m = (\varepsilon_\infty + 2)/(\varepsilon_0 + 2)\tau_0$, while for the Onsager field $\tau_m \simeq \tau_0$ (Onsager, *J. Amer. Chem. Soc.*, 1936, **58**, 1486; Cole, *J. Chem. Phys.*, 1938, **6**, 385). An Onsager field being assumed, the hypothetical molecular volume, V, calculated from τ_0 is 29×10^{-24} ml., compared with the value from the density of 87×10^{-24} ml. With this agreement there are no grounds for suggesting that the reorientating unit is smaller than the whole molecule. The Onsager field is recognised as a poor approximation for an associated liquid like sulphuric acid, but to apply the Kirkwood theory (*J. Chem. Phys.*, 1939, **7**, 911; Oster and Kirkwood, *ibid.*, 1943, **11**, 175) it is essential to know the local liquid structure, or at least the crystal structure, and this has not been measured. It may be noted that Kirkwood's treatment does not automatically predict a high dielectric constant for an associated liquid, because the short-range forces do not necessarily favour parallel orientation of the dipoles, and in an intermediate case the theory leads to the same result as Onsager's. The small value of the distribution parameter α' might be explained

by the fact that the sulphuric acid molecule is not far from spherical (a general correlation between α' and the molecular shape can be established in some systems : Hennelly, Heston, and Smyth, *J. Amer. Chem. Soc.*, 1948, **70**, 4102), but it is equally probable that the distribution of times arises from non-uniformity in the local liquid structure. If the

TABLE 2. *Dispersion and polar relaxation parameters for* H_2SO_4 (20°).
$\varepsilon_0 = 110$; $\varepsilon_\infty = 5$; $\tau_0 = 4{\cdot}8 \times 10^{-10}$ sec.; $\lambda_m = 90$ cm.; $\alpha' = 0{\cdot}085$

relaxation is interpreted as a rate process (Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw-Hill, New York, 1941) in which the rotating molecule crosses a potential barrier from one equilibrium position to another, the usual expression for the free energy of activation can be written

$$\tau_0 = 1/k = (h/kT) \exp (\Delta G_D^{\ddagger}/RT)$$

Similar treatment of viscous flow leads to the relation

$$\eta = (h/v) \exp (\Delta G_v^{\ddagger}/RT) \quad (v = \text{volume per mol.})$$

and from these equations we find $\Delta G_D^{\ddagger} \simeq \Delta G_v^{\ddagger} = 4{\cdot}6$ kcal. per mole at 20°. The agreement probably has no quantitative significance but it supports other evidence for a close relation between the mechanisms of dipole reorientation and viscous flow.

Electrolytic Conductance at High Frequency.—The conductance of anhydrous sulphuric acid is due mainly to the autoprotolysis

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

Both the ions released by this equilibrium have abnormal mobilities (Hammett and Lowenheim, *J. Amer. Chem. Soc.*, 1934, **56**, 2620; Schwab, Zentelis, and Kassapoglou, *Chem. Ber.*, 1952, **85**, 508). Normal ion mobilities are low in sulphuric acid on account of the high viscosity (Hammett and Lowenheim, *loc. cit.*) and there is, therefore, a strong possibility of a large decrease of conductivity if the frequency of the applied field is of the same order of magnitude as the velocity of the proton-exchange process underlying the

TABLE 3. *High-frequency conductivity of aqueous sulphuric acid.*

Medium, H_2SO_4, %	Temp.	λ_0 (cm.)	κ_{20} (ω^{-1} cm.$^{-1}$)	ε_1 *	ε_2 *	Attenuation coeff. (nepers cm.$^{-1}$) exp.	calc.
99·5	21°	304	0·0343	97	28	0·359	0·355
96	21	304	0·1034	97	28	0·642	0·638
100 + KNO_3 (0·27M)	20	304	0·0662	97	28	0·500	0·495
99·5	20	504	0·0345	103	19	0·268	0·273
96	20	504	0·1031	103	19	0·485	0·486
98·7	20	887	0·0554	107	13	0·264	0·267
98·7	20	933	0·0553	107	10	0·267	0·261

abnormal mechanism. According to Hückel (*Z. Elektrochem.*, 1928, **34**, 546) the fall occurs at a wave-length

$$\lambda_c = (4\pi)^2 e a^3 \eta / kT \quad (a = \text{ionic radius}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The average value of a for $H_3SO_4^+$ and HSO_4^- being estimated at 3 Å, λ_c for sulphuric acid is approx. 7 m. A direct test of the theory is possible because the expression for λ_c does not involve an ionic concentration, and λ_c will be primarily unaffected by the addition of a solute. Table 3 contains results for the solutes water (H_3O^+, HSO_4^-) and potassium nitrate (K^+, NO_2^+, $2HSO_4^-$) in the frequency range 30—100 Mc. It will be seen that the electrolytic conductance of these solutions greatly exceeds the dielectrical conductance, so that any dispersion of κ with frequency will be disclosed by an almost proportionate change of the attenuation coefficient. Actually no variation is detected within the experimental limits of accuracy (1—2%).* Similar but less accurate results were obtained at 3000 Mc.

* Values of ε_1 and ε_2 appropriate to the anhydrous acid have been used in calculations of the attenuation coefficient in Table 3 (col. 8). This is not quantitatively correct because the presence of solute will somewhat alter both these quantities (cf. Collie, Hasted, and Ritson, *loc. cit.*) but the changes are secondary compared with the effect of the increased electrolytic conductance, and they also work in opposite directions and tend to cancel.

It is noteworthy that the Hückel effect does not occur in aqueous solutions containing H_3O^+ or OH^- ions at a wave-length of 1·25 cm. although, according to eqn. (5) λ_c = 5—8 cm. A possible explanation (Collie, Hasted, and Ritson, *J. Chem. Phys.*, 1948, **16**, 1) is that the Mosotti field assumed by Hückel should be replaced by an Onsager field, and in sulphuric acid this substitution yields $\lambda_c \simeq 25$ cm. The question of whether the effect occurs at higher frequencies is therefore still open.

A second possibility is the rise of conductivity at high frequency predicted by the Debye–Falkenhagen theory (Falkenhagen, "Electrolytes," Oxford Univ. Press, 1934). Unlike the position with the Hückel effect only a small dispersion of κ is involved and rough calculations indicate that it may be within experimental error. The onset of the dispersion occurs at a wave-length

$$\lambda_f \text{ (cm.)} = 16{\cdot}7\varepsilon_0/\gamma\Lambda_\infty$$

where γ is the electrolyte concentration (g.-equiv./l.) and Λ_∞ is the equivalent conductivity at infinite dilution; the dispersion of conductivity is spread over two decades of frequency, the limiting equivalent conductivity at high frequency being approximately midway between the stationary field value and Λ_∞. Calculations based on the measurements by Schwab and his collaborators (*loc. cit.*) yield λ_f = 170 cm. for anhydrous sulphuric acid, the total dispersion of κ, effective at 1—2-cm. wave-length, being about 1·2%. Moreover, the theoretical Debye–Falkenhagen treatment sets only an upper limit to the dispersion at the ionic strength ($I > 0{\cdot}01$) prevailing in the anhydrous acid; the real effect is probably much smaller (cf. Collie, Hasted, and Ritson, *loc. cit.*).

Electrolyte Solutions in Sulphuric Acid.—Allowance being made for the change of dielectric constant, the thermodynamic properties of electrolyte solutions appear to be essentially the same in sulphuric acid as in water. The semblance of ideality, noted by many workers, is due partly to experimental difficulties (the defects from ideality are never large) and partly to limitations imposed by the solvent, some of which are noted below.

The freezing-point depression constant has been a recurrent difficulty in the interpretation of cryoscopic measurements. A recent determination of the heat of fusion gives k = 6·118 cal. mole^{-1} deg.$^{-1}$ (Rubin and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 800) and this figure is used throughout the calculations in this section. Gillespie, Hughes, and Ingold (*loc. cit.*) adopted a value of 5·98, calculated from freezing-point data for several electrolytes and non-electrolytes on the assumption that the solutes were solvated but otherwise ideal. Hammett and Deyrup (*loc. cit.*) used 6·154, from Brönsted's measurement of the heat of fusion, and earlier workers usually employed higher values, up to 7·0. Cryoscopic measurements in sulphuric acid generally refer to ionic strengths in the range 0·05—0·20, water being added initially to repress the self-ionisation equilibria of the anhydrous acid. The fact that the ionic strengths are high and the range rather limited undoubtedly fosters the impression that the activity coefficients are independent of concentration. Another levelling factor is that the anion in these solutions is necessarily always HSO_4^-.

The most accurate freezing-point data, due to Kunzler and Giauque (*J. Amer. Chem. Soc.*, 1952, **74**, 5271), are for solutions of water in sulphuric acid. Osmotic coefficients calculated from these results in the range of water molality 0·048—0·247 are shown in Fig. 6. The values of g refer to an unsolvated binary electrolyte, allowance being made for the removal of sulphuric acid by the reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

All the points lie higher than predicted by the limiting law, as would be expected for the ionic strengths involved; the important question is whether g is intelligible in terms of one of the extensions of the limiting law valid for aqueous solutions at comparable values of I. For the case of a single 1 : 1 electrolyte the generalised expression proposed by Guggenheim is (*Phil. Mag.*, 1935, **19**, 588)

$$g = 1 - (1/3)am^{\frac{1}{2}}\sigma(m^{\frac{1}{2}}) + \beta m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where m is the electrolyte molality and β is an empirical parameter. For sulphuric acid at 10° ($\varepsilon_0 \sim 115$) the limiting law coefficient is given by

$$(1/3)a = \left(\frac{2\pi N_0 d}{9}\right)^{\frac{1}{2}} \left(\frac{e^2}{\varepsilon_0 kT}\right)^{\frac{3}{2}} = 0{\cdot}324$$

and the limiting law is simply $g = 1 - 0{\cdot}324m^{\frac{1}{2}}$. The full line in Fig. 6 is calculated from eqn. (6) with $\beta = 0$, *i.e.*, with eqn. (6) reduced to the Güntelberg form (*Z. physikal. Chem.*, 1926, **123**, 243), and gives a fairly good representation of the experimental points. Water can therefore be regarded as a " standard " 1 : 1 electrolyte in sulphuric acid; the osmotic coefficients of the solution are quantitatively in agreement with an especially simple extension of the Debye–Hückel theory containing no adjustable parameter. There appear to be no grounds for assuming that a dilute solution of water in sulphuric acid is incompletely ionised, as claimed by Gillespie, Hughes, and Ingold.

Cryoscopic measurements with solutes other than water relate to mixed electrolyte

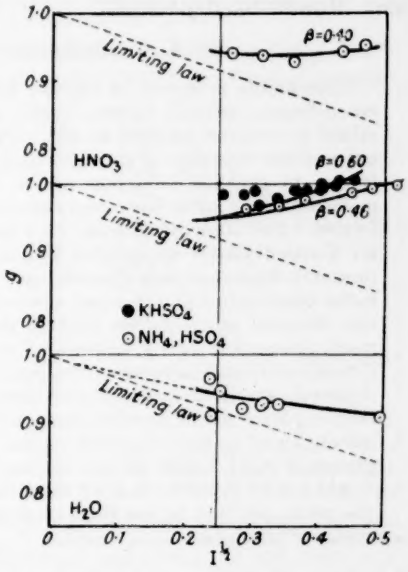


FIG. 6. *Osmotic coefficients of electrolyte solutions in sulphuric acid.*

solutions because the depressions are referred to a slightly aqueous sulphuric acid. In the case where the second solute (R_iHSO_4) is a 1 : 1 electrolyte Guggenheim's equation is

$$g = 1 - (1/3)aI^{\frac{1}{2}}\sigma(I^{\frac{1}{2}}) + \beta_i m_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

it being remembered that β is zero for the first component, $H_3O^+ HSO_4^-$. In eqn. (7) m_i is the molality (as hydrogen sulphate) of the solute R_iHSO_4. Fig. 6 shows the application of eqn. (7) to the cryoscopic results for potassium sulphate, ammonium sulphate, and nitric acid obtained by Gillespie, Hughes, Ingold, and their collaborators. It may be emphasised that the results are given here in the form of *thermodynamic* osmotic coefficients, assumptions regarding solvation or incomplete ionisation being eliminated. The ionisation of nitric acid occurs according to the equation

$$NO_2{\cdot}OH + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

and m_i in eqn. (7) refers to the molality of nitronium hydrogen sulphate. Positive values of β are required to represent the behaviour of these electrolytes but the parameters are within the limits encountered in aqueous solutions. Few, if any, electrolytes in sulphuric acid yield negative values of β. Differences between the osmotic coefficients of the several electrolytes at constant ionic strengths may be due to changes in either

solvation or heat of dilution. The interaction parameters, β, and the deviation of the experimental osmotic coefficients from the eqns. (6) and (7) are summarised below.

Electrolyte	H_3O,HSO_4	NO_2,HSO_4	NH_4HSO_4	$KHSO_4$
β	0·00	0·40	0·46	0·60
Standard deviation (*g*)	+0·009	0·004	0·004	0·008
No. of points	8	5	6	15

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498. *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part II.* The Dipole Moments of the Monohalogeno- and Mononitro-diphenyls.*

By A. C. LITTLEJOHN and J. W. SMITH.

The dipole moments of chloro-, bromo-, and iodo-benzene and of the mono-fluoro-, -chloro-, -bromo-, -iodo-, and -nitro-diphenyls have been determined in benzene solution at 25°. On the assumption that the difference between the moments of corresponding derivatives of benzene and diphenyl is due to classical induction effects only, "theoretical" values for the moments of the latter have been calculated from the measured values for the former. The observed moment for 4-fluorodiphenyl is slightly less, and that for 4-nitrodiphenyl appreciably greater, than the corresponding calculated moments, in accord with the existence of an increased mesomeric effect due to the introduction of the second aromatic ring. For the 3-halogenodiphenyls the observed moments are slightly greater than the calculated values, a result compatible with a suppression of the mesomeric effect of the halogens through conjugation between the rings. The moments of the 2-substituted diphenyls are in all cases greater than the values to be expected with the rings coplanar to one another, and, except for 2-bromodiphenyl, are approximately equal to the calculated values for a configuration with the rings in planes at right angles to one another. As an increased mesomeric effect would not be expected to alter these moments very much, it is inferred that the mean position of the rings is nearer to the perpendicular than to the coplanar arrangement.

THE dipole moments of a number of derivatives of diphenyl have been reported at various times, but the figures show a lack of agreement which renders their interpretation difficult. As an accurate knowledge of the effects on the polarity of the molecule of the introduction of substituents into various positions is of great importance in relation to the spatial arrangement within the molecules and to the character of the central bond, a systematic investigation of the apparent dipole moments of these compounds in benzene solution has been undertaken. In this paper the measurements on the mono-halogeno- and -nitro-diphenyls are reported. As different recorded data for chloro-, bromo-, and iodo-benzene are so much at variance that no satisfactory recalculation of their dipole moments can be carried out, measurements on these compounds have also been included.

Since this work was begun, Everard, Kumar, and Sutton (*J.*, 1951, 2807) have reported measurements on 4-bromo- and 4-nitro-diphenyl, and Everard and Sutton (*J.*, 1951, 2817) have tabulated and discussed the available data for the mono-chloro-, -nitro-, -amino-, and -cyano-diphenyls. Although the results included in this comparison were recalculated by Halverstadt and Kumler's method (*J. Amer. Chem. Soc.*, 1941, **64**, 2982), the original data were drawn from several sources, and in certain instances the figures derived differ appreciably from ours.

* Part I, Beaven, Hall, Lesslie, and Turner, *J.*, 1952, 854.

The essential parameters and the values of $P_{2\infty}$, $[R_D]$, and μ derived from them are listed in Table 1, where α, β, and ν denote the limiting values of $\Delta\epsilon/w$, $\Delta v/w$, and $\Delta n^2/w$, respectively, at zero concentration, and the other symbols have their usual significance. To facilitate comparison with previous measurements, and with the summary drawn up by Everard and Sutton, the dipole moments have been calculated on the assumption that P_{E+A} is represented sufficiently closely by $[R_D]$. This has some justification in the present instance since Le Fèvre and Le Fèvre (*J.*, 1936, 487) found that $P_{2\infty} \simeq [R_D]$ for diphenyl and for 4 : 4'-dichlorodiphenyl. The previous values recorded all refer to measurements in benzene solution.

The moment now found for chlorobenzene supports the majority of the earlier measurements rather than the slightly higher value reported by Le Fèvre and used by Everard and Sutton in their comparisons. Of the other compounds which had been studied previously, the greatest deviation from earlier values occurs with 2-nitrodiphenyl. The reason is obscure, but the presence of isomers in the sample used would have been expected to cause the result to be higher than previous values, rather than lower, as is found.

TABLE 1. *Polarisation data for solutions in benzene at* 25°.

Compound	$10^3\alpha$	$-10^4\beta$	$10^3\nu$	$P_{2\infty}$ (c.c.)	$[R_D]$ (c.c.)	μ (D.)	Previous values
Diphenyl derivatives.							
2-Fluoro ...	1,346	2514	196	89·4	51·6	1·36	
3-Fluoro ...	1,730	2490	195	102·0	51·6	1·57	
4-Fluoro ...	1,589	2484	210	97·4	52·1	1·49	1·50 [a]
2-Chloro ...	1,409	2808	256	98·5	57·2	1·42	1·30 [b], 1·44 [c], 1·45 [d]
3-Chloro ...	1,820	2847	283	112·9	57·6	1·65	1·79 [b], 1·64 [d]
4-Chloro ...	1,850	2846	286	114·0	57·8	1·66	1·58 [a], 1·53 [b], 1·63 [c], 1·63 [d], 1·64 [e]
2-Bromo ...	1,279	4159	248	106·7	60·8	1·50	
3-Bromo ...	1,506	4345	263	115·1	60·2	1·64	
4-Bromo ...	1,539	4343	267	116·8	60·3	1·66	1·64 [a], 1·65 [f]
2-Iodo ...	897	5119	284	100·0	67·1	1·27	
3-Iodo	1,110	5245	295	110·2	66·7	1·46	
4-Iodo ...	1,110	5313	312	109·7	67·0	1·45	
2-Nitro ...	7,720	3237	285	338·0	58·8	3·70	3·80 [a], 3·79 [c], 3·81 [e], 3·82 [g]
3-Nitro ...	9,523	3330	301	405·0	58·7	4·12	3·90 [c]
4-Nitro ...	10,670	3367	333	447·7	59·7	4·36	4·17 [a], 4·28 [c], 4·41 [f]
Benzene derivatives.							
Chloro ...	2,450	2328	68	82·4	31·5	1·58	1·53—1·64 [h], 1·60 [i]
Bromo	1,778	4711	129	84·0	34·1	1·56	1·48—1·58 [h], 1·55 [j], 1·57 [e]
Iodo	1,198	5949	175	79·4	39·5	1·40	1·25 [k], 1·295 [l], 1·38 [m], 1·42 [n]

[a] Le Fèvre and Le Fèvre, *J.*, 1936, 1130. [b] Weissberger and Sangewald, *Z. physikal. Chem.*, 1933, **20**, *B*, 145. [c] Naeshagen, *ibid.*, 1934, **25**, *B*, 157. [d] Hampson and Weissberger, *J. Amer. Chem. Soc.*, 1936, **58**, 2111. [e] Recalc. from previous data by Everard and Sutton, *J.*, 1951, 2817. [f] Everard, Kumar, and Sutton, *J.*, 1951, 2807. [g] Lumbroso, *Bull. Soc. chim.*, 1949, **16**, D387. [h] Various measurements prior to 1947, from Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948. [i] Le Fèvre, *Trans. Faraday Soc.*, 1950, **46**, 1. [j] Brown and de Vries, *J. Amer. Chem. Soc.*, 1951, **73**, 1811. [k] Walden and Werner, *Z. physikal. Chem.*, 1929, **2**, *B*, 10. [l] Bergmann, Engel, and Sandor, *ibid.*, 1930, **10**, *B*, 106. [m] Tiganik, *ibid.*, 1931, **13**, *B*, 425. [n] Saxby, quoted by Everard and Sutton, *loc. cit.*

The molecular refractions deduced from the measurements on the solutions are generally close to those for the liquid state and to the values calculated by adding the difference between the molecular refraction of diphenyl (52·41 c.c.; von Auwers and Frühling, *Annalen*, 1921, **422**, 192) and benzene (26·21 c.c.) to the molecular refractions of the corresponding benzene derivatives (Vogel, Cresswell, Jeffrey, and Lester, *J.*, 1952, 514), *viz.*, fluoro- 52·18, chloro- 57·34, bromo- 60·19, iodo- 65·35, and nitro-diphenyl 58·92 c.c.

Everard and Sutton (*J.*, 1951, 2821) have discussed in detail the interactions between a substituent group and the aryl radical to which it is linked. These comprise: (*a*) the inductive effect, arising through polarisation of the radical by the electric field of the substituent, and now regarded as itself being the result of two components, namely, (i) the "classical" inductive effect (I_C), a purely electrostatic process influencing both σ- and π-electrons, and (ii) the "non-classical" inductive effect (I_X), leading to changes of π-bond order; and (*b*) the mesomeric effect arising through the tendency towards the formation of

a π-bond between the substituent and the carbon atom to which it is linked, and causing modifications in the character of the other bonds present in the radical.

From electrostatic theory the I_C effect decreases as the inverse cube of the distance from a point dipole, and hence it is of relatively short range. The I_N effect, however, influences the whole of a conjugated system, and so becomes very closely associated with the mesomeric effect, although, like the I_C effect it may either reinforce or oppose the latter. As changes in π-electron distribution have a reciprocal effect in modifying the σ-bonds between the carbon atoms and the substituent group, and between one carbon atom and another, the whole problem is rather complex.

As the measurements on derivatives of diphenyl have been made in solution, the dipole moments deduced from them are modified by an unknown solvent effect. Hence no exact correlation between theory and observation can be expected, but as benzene was the solvent in all the determinations these solvent effects may be expected to be approximately proportional to the moments of the primary dipoles in these analogous series of compounds. Hence it is interesting to correlate these observations with those on the corresponding benzene derivatives in the same solvent.

Everard and Sutton (*J.*, 1951, 2818) have retained the original definition of the " mesomeric moment " of an aromatic compound as the vector difference between its dipole moment and that of its aliphatic analogue (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668). The mesomeric moments, in this sense, of the 4-substituted diphenyl compounds are compared with those of the benzene analogues in Table 2, where the convention adopted is that a positive sign indicates that the moment of the aromatic compound is less than that of its aliphatic analogue.

TABLE 2. *Mesomeric moments* (D) *of 4-substituted compounds.*

Substituent	F	Cl	Br	I	NO_2
Benzene compound	+0·41	+0·43	+0·44	+0·53	−0·76
Diphenyl compound	+0·40	+0·37	+0·34	+0·47	−1·11

As the moments of the C–X σ-bonds cannot differ appreciably between the two series, the differences between the mesomeric moments must be due to the combined action of the I_C and the I_N effect and of the true mesomeric effect. For nitro-compounds the effects all operate in the same sense and hence lead to an increase of 0·35 D in the mesomeric moment on addition of a second ring. For the halogeno-compounds, however, the inductive effects operate in the opposite sense to the mesomeric effect, with the result that when the second ring is added they appear to cancel one another in 4-fluorodiphenyl, whilst the inductive effects outweigh any increased mesomeric effect for the other halogeno-derivatives.

These results, however, do not permit any estimation of the relative magnitudes of the various effects, so it is of interest to calculate the extent to which the differences between the observed moments of the diphenyl and benzene compounds can be interpreted on the basis of the classical inductive effect.

According to the theory developed by Smallwood and Herzfeld (*J. Amer. Chem. Soc.*, 1930, **52**, 1919) and by Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) the components of the induced moment μ_x and μ_y, respectively parallel to and at right angles to the inducing moment μ, are given by

$$\mu_x = \mu\alpha \cdot \frac{\varepsilon_a + 2}{3\varepsilon_b r^3}(3\cos^2\theta - 1); \quad \mu_y = \mu\alpha \cdot \frac{\varepsilon_a + 2}{3\varepsilon_b r^3} \cdot 3\sin\theta\cos\theta,$$

where α is the polarisability of the polarisable system, ε_a and ε_b are the dielectric constants of the polarisable system and of the medium between this and the primary dipole, respectively, r is the distance between the dipole and the polarisable centre, and θ is the angle between μ and r. According to the method by which this theory was applied by Hampson and Weissberger to naphthalene compounds (*J.*, 1936, 393) and to the chlorodiphenyls (*J. Amer. Chem. Soc.*, 1936, **58**, 2111), and by Le Fèvre and Le Fèvre to a few derivatives of diphenyl (*J.*, 1936, 1130), a mono-substituted diphenyl molecule may be regarded as the

corresponding derivative of benzene to which an additional polarisable group, namely, a benzene ring, has been added. The polarisable centre of this additional group is at the middle of the unsubstituted ring, and α is the polarisability of benzene, *i.e.*, $12{\cdot}5 \times 10^{-24}$ in the plane of the ring and $6{\cdot}25 \times 10^{-24}$ at right angles to that plane (Debye, "Handbuch der Radiologie," Akademische Verlagsges., Leipzig, 1925, Vol. VI, 786). No great error can be introduced by taking both ε_a and ε_b as 2·27, the dielectric constant of benzene.

The inducing dipole has been assumed in each case to be equal to the dipole moment of the corresponding benzene derivative as measured in benzene solution. The error due to regarding this as a point dipole cannot be large so long as the dipole is at some distance from the polarisable centre.

As the moment of a halogeno-compound probably includes contributions in the sense $\overset{-}{\text{C}}\,\overset{+}{\text{X}}$ from both the σ- and the π-bonding orbitals, which are more than offset by the moment in the reverse sense due to the lone-pair electrons of the halogen atom, it follows that the "centre" of the electrical asymmetry will lie somewhere between the two nuclei. For the halogen compounds it has been taken as located at the "point of contact" of the carbon and the halogen atoms, *i.e.*, on the C–X bond and 0·77 Å from the carbon nucleus. For the nitrodiphenyls it has been taken as at the centre of the nitrogen atom. The internuclear distances used have been C–C (aromatic) 1·40, C–C (centre bond) 1·50, and C–N 1·45 Å.

When the rings are coplanar, and for all orientations when a symmetrical substituent is in the 4-position, the inducing field and induced moment are in the plane of the ring, and hence the value of α for the plane of the ring is applicable. On the other hand, when the rings are not coplanar and the substituent is in the 2- or the 3-position the field set up must be resolved in directions parallel to and at right angles to the plane of the unsubstituted ring, and the appropriate values of α used in each case. As the polarisability is less in the direction at right angles to the ring, the effect of the induced moment on the overall moment decreases progressively with increasing angle of inclination of the planes of the rings, and becomes a minimum for the right-angled position. The values of r and θ calculated for the various types of diphenyl compounds discussed are recorded in Table 3, together with the theoretical ratios of the moments of the corresponding diphenyl and benzene derivatives for the two extreme positions of the rings, *i.e.*, coplanar, and in planes at right angles.

TABLE 3.

			μ (calc.)/μ (benzene derivative)	
	r	θ	Rings coplanar	Rings at 90°
2-Halogenodiphenyl	3·73	89° 32′	0·849	0·906
3-Halogenodiphenyl	5·71	40° 41′	1·032	1·034
4-Halogenodiphenyl	6·47	0°	1·058	1·058
2-Nitrodiphenyl	3·79	79° 3′	0·876	0·908
3-Nitrodiphenyl	6·25	33° 34′	1·031	1·030
4-Nitrodiphenyl	7·17	0°	1·042	1·042

To derive calculated figures for comparison with the observed values the dipole moment of fluorobenzene has been taken as 1·48 D, the value used by Everard and Sutton. The moments of chloro-, bromo-, and iodo-benzene have been remeasured, whilst for nitrobenzene the value of $P_{2\infty}$ at 25° (362·0 c.c.) recalculated by Cleverdon and Smith (*Trans. Faraday Soc.*, 1949, **45**, 109) has been used in conjunction with $P_{E+A} = [R_D] = 32{\cdot}7$ c.c. to compute μ.

The observed and calculated values of the dipole moments of the diphenyl derivatives are compared in Table 4, in which the figure for 4-cyanodiphenyl reported by Everard, Kumar, and Sutton (*loc. cit.*) is also included.

The measured moments of 4-nitro- and 4-cyano-diphenyl are appreciably greater than the calculated values. For these compounds the I_N effect operates in the same sense as the mesomeric effect, each tending to increase the moment. The results, therefore, lead to the inference that the resultant of these two effects is increased considerably by introducing the second ring, indicating that the effects are transmitted through the central bond linking the two rings.

For the 4-halogenodiphenyls, however, the I_N effect operates in the reverse sense to the mesomeric effect, the former tending to increase the dipole moment and the latter to decrease it. For 4-fluorodiphenyl the mesomeric effect seems to be predominant, but in the other compounds of this class the two effects appear virtually to cancel one another. As the moment of the primary dipole in 4-fluorodiphenyl is about 0·1 D smaller than in 4-chloro- or in 4-bromo-diphenyl, the inductive effect will be slightly less than in either of the latter compounds, so the fact that the observed moment is 0·08 D less than the calculated value may be evidence of the greater mesomeric effect of fluorine compared with other

TABLE 4. *Comparison of observed with calculated dipole moments for diphenyl derivatives.*

	μ obs. (D)	μ calc. (D)	Difference (D)		μ obs. (D)	μ calc. (D)	Difference (D)
2-Fluorodiphenyl	1·36	1·26 (coplanar)	+0·10	3-Fluorodiphenyl...	1·57	1·53	+0·04
		1·34 (90°)	+0·02	3-Chlorodiphenyl...	1·65	1·63	+0·02
2-Chlorodiphenyl	1·42	1·34 (coplanar)	+0·08	3-Bromodiphenyl...	1·64	1·61	+0·03
		1·43 (90°)	−0·01	3-Iododiphenyl ...	1·46	1·45	+0·01
2-Bromodiphenyl	1·50	1·32 (coplanar)	+0·18	3-Nitrodiphenyl ...	4·12	4·13	−0·01
		1·41 (90°)	+0·09	4-Fluorodiphenyl...	1·49	1·57	−0·08
2-Iododiphenyl ...	1·27	1·19 (coplanar)	+0·08	4-Chlorodiphenyl...	1·66	1·67	−0·01
		1·27 (90°)	0·0	4-Bromodiphenyl...	1·66	1·65	+0·01
2-Nitrodiphenyl	3·70	3·51 (coplanar)	+0·19	4-Iododiphenyl ...	1·45	1·48	−0·03
		3·64 (90°)	+0·06	4-Nitrodiphenyl ...	4·36	4·18	+0·18
				4-Cyanodiphenyl ...	4·33	4·22	+0·11

halogen atoms. For the other 4-halogenodiphenyls the differences between the observed and the calculated values are within the possible errors of computation arising from the incidence of solvent effect and atom polarisation.

If conjugation occurs across the bond between the two nuclei, the introduction of a phenyl group into the 3-position of a benzene derivative would be expected to decrease slightly the mesomeric effect of a halogen atom, and to increase slightly that of a nitro-group. The differences between the observed and the calculated moments for the 3-substituted diphenyl derivatives are small, and within the possible errors referred to above, but in each case they are in the sense expected from the modification in mesomeric effect, and hence are not incompatible with conjugation between the rings.

The evidence of the measurements on the 4- and 3-substituted derivatives of diphenyl is therefore in general confirmation of the conclusion reached from a number of different approaches to the problem, both chemical and physical, that in the diphenyl skeleton conjugation occurs through the central bond (cf. Part I, *loc. cit.*).

In 2-substituted diphenyl derivatives an increased mesomeric effect should lead to electron drifts along the axis of the dipole and in a direction at 120° to this axis. The resultant effect upon the dipole moment of the moment would therefore be expected to be small. As, with the possible exception of 2-fluorodiphenyl, it is impossible on steric grounds for any of these molecules to assume a fixed coplanar configuration, their dipole moments would be expected to lie between the values calculated for the coplanar and the right-angled positions of the rings. The observed moments are much greater than the values calculated for the coplanar position, and, except for 2-bromodiphenyl, the value for which is anomalously high, they all lie near the figures calculated for the perpendicular configuration. Although for the latter configuration the calculated inductive effect does not depend very critically upon the exact location assumed for the point dipole, the polarisable centres are much nearer to the dipole in these compounds than in the 3- and 4-substituted derivatives. I_C effects almost identical with those used are obtained if the unsubstituted ring is regarded as six polarisable centres located either at the carbon nuclei or at the mid-points of the C–C bonds, instead of as a polarisable whole, but the assumption of a point dipole may lead to some error in this case. Therefore, beyond the general inference that the mean position of the rings in these compounds is probably much nearer the right-angled than the coplanar position, it is not justifiable to draw further conclusions from the small differences between the observed and the calculated figures.

Experimental

Preparation and Purification of Materials.—" Crystallisable "-grade benzene was purified as described by Few and Smith (*J.*, 1949, 753). All batches were of constant b. p. within ±0·02°; d_4^{25} 0·87368 ± 0·00003; n_D^{25} 1·4980 ± 0·0001 (" Selected Values of the Properties of Hydrocarbons," American Petroleum Institute, 1948, gives d_4^{25} 0·87370, n_D^{25} 1·49791).

2- and 4-Nitrodiphenyl were prepared by Bell, Kenyon, and Robinson's method (*J.*, 1926, 1242), the former being purified by Gull and Turner's method (*J.*, 1929, 491). These and all other solid compounds were recrystallised to constant m. p. (38° and 114°, respectively; lit., 35—38° and 113—114°).

3-Nitrodiphenyl, prepared by Elks, Haworth, and Hey's method (*J.*, 1940, 1284) and recrystallised successively from light petroleum (b. p. 40—60°) and alcohol, had m. p. 60·5° (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339, and Elks, Haworth, and Hey, give 61°).

Aminodiphenyls were prepared by reducing the nitrodiphenyls with iron filings and water in the presence of a trace of acetic acid, the product being made alkaline with ammonia and extracted with acetone. These were converted into the fluorodiphenyls by Schiemann and Roselius's method (*Ber.*, 1929, **62**, 1805), the products being recrystallised from alcohol. 2-, 3-,

Table 5.

100*w*	ε	*v*	*n*	100*w*	ε	*v*	*n*
	2-*Fluorodiphenyl* (*sample* i)				4-*Fluorodiphenyl*		
0·0000	2·2725	1·14459	1·4980	0·0000	2·2725	1·14454	1·4981
1·0632	2·2868	1·14195	1·4987	0·5190	2·2806	1·14330	1·4984
1·8077	2·2969	1·14006	1·4991	1·1198	2·2903	1·14175	1·4989
2·3776	2·3047	1·13857	1·4994	1·6251	2·2984	1·14050	1·4992
2·8719	2·3113	1·13742	1·4999	2·2328	2·3079	1·13901	1·4996
3·7650	2·3234	1·13514	1·5006	2·6494	2·3142	1·13796	1·5000
4·6775	2·3356	1·13280	1·5012	2·9683	2·3192	1·13713	1·5002
				3·4652	2·3269	1·13590	1·5006
	2-*Fluorodiphenyl* (*sample* ii)				3-*Chlorodiphenyl*		
0·0000	2·2725	1·14462	1·4980	0·0000	2·2725	1·14462	1·4980
1·0240	2·2860	1·14205	1·4987	0·8622	2·2885	1·14216	1·4988
1·5003	2·2927	1·14082	1·4989	1·3345	2·2968	1·14082	1·4993
1·8791	2·2975	1·13987	1·4992	1·4790	2·2994	1·14040	1·4994
3·0648	2·3137	1·13691	1·5000	2·2495	2·3136	1·13821	1·5001
				2·9636	2·3267	1·13618	1·5008
	2-*Chlorodiphenyl*			3·9578	2·3450	1·13337	1·5019
0·0000	2·2725	1·14459	1·4980				
1·0334	2·2874	1·14167	1·4988		2-*Bromodiphenyl*		
1·5409	2·2940	1·14028	1·4991	0·0000	2·2725	1·14462	1·4979
2·1712	2·3034	1·13845	1·4996	1·1689	2·2877	1·13977	1·4989
2·4536	2·3075	1·13774	1·4999	1·8598	2·2964	1·13680	1·4995
3·1671	2·3167	1·13573	1·5004	2·8137	2·3084	1·13297	1·5002
3·5204	2·3216	1·13471	1·5009	3·6557	2·3190	1·12948	1·5009
4·3726	2·3342	1·13222	1·5017	4·0959	2·3252	1·12742	1·5013
				4·6656	2·3294	1·12532	1·5017
	4-*Chlorodiphenyl*				3-*Bromodiphenyl*		
0·0000	2·2725	1·14461	1·4980	0·0000	2·2725	1·14452	1·4980
0·9463	2·2903	1·14198	1·4989	1·3745	2·2932	1·13858	1·4992
1·6477	2·3028	1·13997	1·4996	2·1059	2·3044	1·13524	1·4998
2·1235	2·3117	1·13857	1·5001	2·9722	2·3174	1·13171	1·5006
2·6418	2·3211	1·13710	1·5006	3·2150	2·3220	1·13060	1·5008
3·0548	2·3292	1·13590	1·5010	4·1031	2·3347	1·12670	1·5015
3·5108	2·3378	1·13459	1·5013	4·7750	2·3452	1·12368	1·5023
4·9308	2·3634	1·13056	1·5025	5·2729	2·3539	1·12164	1·5027
	3-*Fluorodiphenyl*				2-*Iododiphenyl*		
0·0000	2·2725	1·14462	1·4980	0·0000	2·2725	1·14462	1·4980
1·1203	2·2917	1·14184	1·4988	0·8993	2·2808	1·14001	1·4988
1·6617	2·3014	1·14046	1·4991	1·4505	2·2858	1·13717	1·4994
2·2278	2·3111	1·13904	1·4994	2·0141	2·2919	1·13426	1·4999
2·4626	2·3156	1·13846	1·4996	2·6443	2·2978	1·13108	1·5004
3·2667	2·3291	1·13654	1·5001	3·0305	2·3024	1·12912	1·5009
3·3654	2·3314	1·13621	1·5002	3·2094	2·3030	1·12824	1·5011
4·4766	2·3503	1·13352	1·5009	3·9546	2·3119	1·12440	1·5018

TABLE 5.—*Continued.*

100*w*	ε	*v*	*n*	100*w*	ε	*v*	*n*
	4-*Iododiphenyl*				4-*Nitrodiphenyl*		
0·0000	2·2725	1·14462	1·4980	0·0000	2·2725	1·14459	1·4980
1·0507	2·2843	1·13902	1·4991	1·1622	2·3968	1·14069	1·4993
1·3481	2·2873	1·13754	1·4994	1·5389	2·4381	1·13933	1·4997
2·0467	2·2956	1·13378	1·5001	2·1324	2·5031	1·13743	1·5003
2·4159	2·2996	1·13176	1·5005	2·4178	2·5343	1·13423	1·5007
3·0618	2·3075	1·12833	1·5012	3·0743	2·6059	1·13423	1·5013
3·6434	2·3142	1·12527	1·5018	3·5503	2·6582	1·13266	1·5020
				4·3400	2·7470	1·13000	1·5029
	3-*Nitrodiphenyl*				*Chlorobenzene*		
0·0000	2·2725	1·14459	1·4980	0·0000	2·2725	1·14462	1·4977
1·0458	2·3726	1·14108	1·4990	0·9667	2·2960	1·14237	1·4979
1·5716	2·4233	1·13935	1·4996	1·4006	2·3071	1·14131	1·4980
1·9760	2·4626	1·13800	1·5000	2·1528	2·3254	1·13958	1·4982
2·4938	2·5130	1·13633	1·5005	3·0452	2·3478	1·13757	1·4984
2·9697	2·5597	1·13471	1·5010	4·0086	2·3723	1·13533	1·4986
3·2971	2·5917	1·13364	1·5013	5·3106	2·4050	1·13226	1·4989
4·1664	2·6775	1·13068	1·5022				
	4-*Bromodiphenyl*				*Iodobenzene*		
0·0000	2·2725	1·14459	1·4980	0·0000	2·2725	1·14462	1·4980
0·5154	2·2806	1·14239	1·4984	1·1250	2·2860	1·13792	1·4987
1·2248	2·2914	1·13926	1·4991	1·8641	2·2949	1·13357	1·4991
1·7120	2·2989	1·13715	1·4995	2·4291	2·3015	1·13015	1·4994
1·9057	2·3018	1·13629	1·4997	3·1596	2·3103	1·12587	1·4999
2·4967	2·3107	1·13371	1·5002	4·6528	2·3285	1·11691	1·5007
3·0626	2·3196	1·13135	1·5008	5·5135	2·3384	1·11181	1·5012
				6·7262	2·3541	1·10459	1·5019
	3-*Iododiphenyl*				*Bromobenzene*		
0·0000	2·2725	1·14462	1·4980	0·0000	2·2725	1·14462	1·4980
1·0788	2·2849	1·13897	1·4990	0·6423	2·2838	1·14161	1·4982
1·4705	2·2893	1·13694	1·4995	0·1847	2·2867	1·14087	1·4984
2·0026	2·2952	1·13403	1·5000	1·2156	2·2942	1·13890	1·4985
2·8073	2·3043	1·12984	1·5008	1·7062	2·3029	1·13663	1·4987
3·4686	2·3119	1·12646	1·5014	1·8568	—	1·13577	1·4988
3·7644	2·3146	1·12489	1·5017	2·7268	2·3209	1·13175	—
4·9218	2·3273	1·11885	1·5028	3·3684	—	1·12834	1·4992
				4·4817	2·3532	1·12327	—
	2-*Nitrodiphenyl*			5·2954	—	1·11954	1·4999
0·0000	2·2725	1·14459	1·4980	7·2217	—	1·11043	1·5005
0·9915	2·3477	1·14139	1·4990	8·6312	—	1·10371	1·5012
1·2801	2·3716	1·14048	1·4992				
2·1704	2·4409	1·13761	1·5001				
2·5328	2·4684	1·13636	1·5004				
3·0716	2·5111	1·13459	1·5009				
3·4107	2·5378	1·13355	1·5012				

and 4-Fluorodiphenyl had m. p. 74·5°, 29·5°, and 75°, respectively (Schiemann and Roselius gave 72°, 26—26°, and 74—75°, respectively).

Chlorodiphenyls were prepared by Sandmeyer's method (Zaheer and Faseeh, *J. Indian Chem. Soc.*, 1944, **21**, 27), the 2- and 3-isomers being fractionally distilled at reduced pressure. 2- and 4-Chlorodiphenyl, recrystallised from alcohol, had m.p. 32·5° and 77°, respectively (lit., 31—34° and 75·5—77·7°). 3-Chlorodiphenyl had d_4^{25} 1·1579, n_D^{25} 1·6181, $[R_D]$ 57·1 c.c.

2-Bromodiphenyl was prepared by Sandmeyer's method, the diazotisation being effected in hydrobromic acid, and the product was fractionally distilled at low pressure. It had d_4^{25} 1·3522, n_D^{25} 1·6248, $[R_D]$ 60·9 c.c.

3-Bromodiphenyl, prepared by Huber, Renoll, Rossow, and Mowry's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1109), had d_4^{25} 1·3976, n_D^{25} 1·6385, $[R_D]$ 60·0 c.c. (Huber *et al.* give n_D^{25} 1·6390).

4-Bromodiphenyl, lent by Professor Turner and recrystallised from alcohol, had m. p. 90·5° (lit., 89—91·2°).

Iododiphenyls were prepared by diazotising the corresponding amines and adding the products to potassium iodide solution. 2-Iododiphenyl, isolated by extraction with ether, had d_4^{25} 1·5511, n_D^{25} 1·6548, $[R_D]$ 66·2 c.c. 3-Iododiphenyl, isolated by Campaigne and Reid's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1663), had d_4^{25} 1·5967, n_D^{25} 1·6730, $[R_D]$ 65·8 c.c. 4-Iododiphenyl, recrystallised from acetic acid, had m.p. 114° (lit., 112—114°).

Apparatus and Measurements.—The dielectric constants were determined relative to benzene as standard, with a heterodyne beat apparatus (Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211). Specific volumes were measured with a pyknometer, and the refractive indices with a Hilger Abbé refractometer. All measurements were made at 25·0°.

The results from which the parameters listed in Table 1 were derived are summarised in Table 5, where the symbols have their usual significance. For many of the compounds the dielectric constants of the solutions were linear with w over the concentration range studied, and hence the slope of the best straight line through these values was taken as α. For the nitrodiphenyls, however, the variation of ε with w was not linear, and hence the limiting value of $\delta\varepsilon/\delta w$ at low concentration was used. In all cases both v and n^2 were linear with w, and the slopes of the best straight lines were taken for β and ν, respectively. The values of $P_{2\infty}$ deduced from these parameters were in each case checked with the result of plotting against w the values of P_2 calculated from the data for each concentration, and extrapolating to zero concentration. The values of $[R_D]$ were similarly checked against the values derived for the individual concentrations.

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499. *The Synthesis of Emetine and Related Compounds. Part II.* The Synthesis of (±)-Rubremetinium Bromide.*

By ALAN R. BATTERSBY, H. T. OPENSHAW, and HAMISH C. S. WOOD.

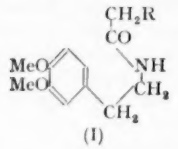
The hexahydro-oxoquinolizine derivative (V) has been synthesised from (I; R = CO_2Et or CN) and converted by two methods into (±)-rubremetinium bromide. The structural identity of the product with (+)-rubremetinium bromide derived from emetine has been shown spectroscopically, thus confirming the structure of the alkaloid.

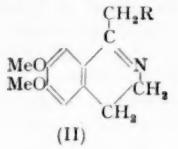
IN Part I * we gave a preliminary account of the confirmation of the structure of emetine by the total synthesis of (±)-rubremetinium bromide. We now describe this synthesis in full, together with an improved method.

3 : 4-Dimethoxyphenethylamine reacts with ethoxycarbonylacetyl chloride, or more conveniently with excess of ethyl malonate at 125°, to give ethyl *N*-3 : 4-dimethoxyphenethylmalonamate (I; R = CO_2Et), which is cyclised by phosphoric oxide to ethyl 3 : 4-dihydro-6 : 7-dimethoxy-1-*iso*quinolylacetate (II; R = CO_2Et), but this compound is prepared most satisfactorily by Osbond's method (*J.*, 1951, 3464). It is hydrogenated smoothly to the tetrahydro*iso*quinoline (III). Two methods were investigated for the conversion of (III) into (IV). In spite of unfavourable indications in the literature (see, for example, Philippi and Galter, *Monatsh.*, 1929, **51**, 253) piperidine was found to add smoothly to ethyl α-ethylacrylate, yielding ethyl 1-piperidinobutane-2-carboxylate, but the reaction of (III) with the acrylate was complex and did not lead to the desired product. Condensation of (III) with ethyl α-formylbutyrate, followed by hydrogenation (cf. Décombe, *Ann. Chim.*, 1932, **18**, 81), effected partial conversion into (IV), and repetition of the process gave an acceptable yield. Dieckmann cyclisation followed by acid hydrolysis led to the oxoquinolizine derivative (V) in good yield. The ketone (V) contains two asymmetric centres, but since one of these is adjacent to the carbonyl group and may readily suffer inversion through enolisation, the single crystalline isomer isolated is probably the more stable form. The slow deposition of further crops of pure crystalline ketone from the mother-liquors may be due to inversion of small amounts of the less stable isomer contained in them.

* A paper by Battersby and Openshaw in *Experientia*, 1950, **6**, 387, is considered as Part I.

McElvain and Lyle (*J. Amer. Chem. Soc.*, 1950, **72**, 384) have shown that 1-methyl-4-piperidone condenses with ethyl cyanoacetate, and we have successfully converted the condensation product by hydrolysis, hydrogenation, and esterification into ethyl 1-methyl-


(I)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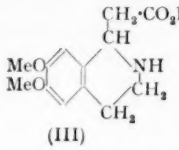
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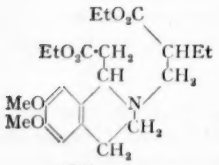
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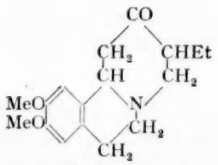
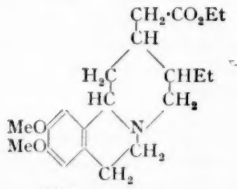
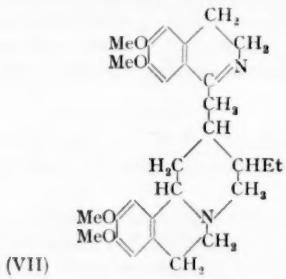
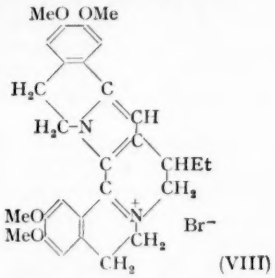

(V)


(VI)

4-piperidylacetate. By applying a similar procedure to the ketone (V), the ester (VI) was obtained, although not in an analytically pure condition. It was heated with 3 : 4-dimethoxyphenethylamine, and the product was cyclised with phosphoryl chloride. The resulting mixture of bases yielded no crystalline derivatives, but it was shown to contain the expected product (VII), structurally identical with *O*-methylpsychotrine, since oxidation with mercuric acetate gave a small amount of (±)-rubremetinium bromide (VIII). This product had an ultra-violet and visible absorption spectrum identical with that of (+)-rubremetinium bromide obtained by similar oxidation of emetine (Part I, *loc. cit.*).

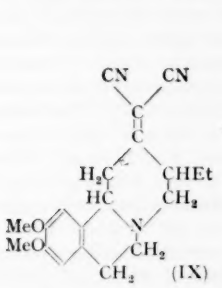

(VII)


(VIII)

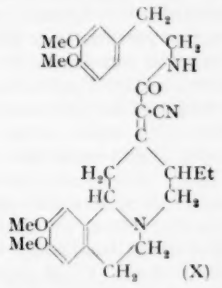
The very poor yield obtained in the above synthesis, and the failure to obtain pure crystalline products beyond the stage of the ketone (V), led us to seek improvements in the later stages, particularly as our ultimate aim is the synthesis of a product having the correct stereochemical configuration as well as the structure of emetine.

The ketone (V) was found to condense with malononitrile to give a crystalline product (IX) in excellent yield, but attempts to hydrogenate and to hydrolyse this substance gave unsatisfactory results. 1-Cyanomethyl-3 : 4-dihydro-6 : 7-dimethoxy*iso*quinoline (II; R = CN) possesses a methylene group situated very similarly to that of malononitrile, but a series of model experiments (Morgan and Openshaw, forthcoming paper) showed that it cannot be condensed with ketones. Its precursor, α-cyano-*N*-3 : 4-dimethoxyphenethylacetamide (I; R = CN), however, condenses smoothly with ketones, and the products, after hydrogenation, can be cyclised to dihydro*iso*quinolines. When this process was applied to the ketone (V), a crystalline condensation product (X) was obtained in satisfactory yield. Attempted cyclisation of this product with phosphoric oxide led to its breakdown, the only product isolable after hydrolysis being 3 : 4-dihydro-6 : 7-dimethoxy-1-methyl*iso*quinoline. Hydrogenation of (X) gave a crystalline dihydro-compound (XI), cyclisation of which was effected by phosphoric oxide in boiling *pseudo*cumene (lower

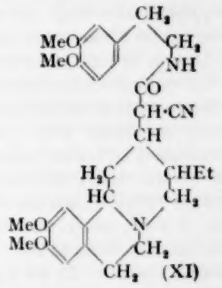
temperatures were ineffective), and after hydrolysis and decarboxylation the crude base (VII) was obtained in about 33% yield. On oxidation with mercuric acetate a 25% yield of (±)-rubremetinium chloride was obtained. Comparison with the maximum yield



(IX)

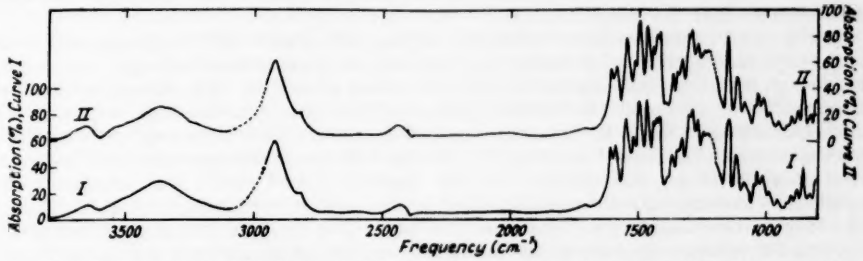


(X)



(XI)

(45%) obtained in the oxidation of emetine (Battersby and Openshaw, *J.*, 1949, S 67) suggests that the crude base contained over 50% of the expected product (VII). The (±)-rubremetinium chloride, after further purification, was converted into the bromide, which was shown to be structurally identical with (+)-rubremetinium bromide by a comparison of the infra-red absorption spectra (see Figure) of their chloroform solutions.



Infra-red absorption in chloroform. I, "Natural" (+)-rubremetinium bromide. II, Synthetic (±)-rubremetinium bromide. (Broken lines indicate zones of strong solvent absorption.)

While the work described in this paper was in progress, Preobrashenski and his co-workers (*Doklady Akad. Nauk*, S.S.S.R., 1950, **75**, 539; 1951, **81**, 421) gave a preliminary account of a complete synthesis of emetine, but full details, particularly of the separation of the various stereoisomers which would be expected, do not appear to have been published yet. Pailer and Strohmayer (*Monatsh.*, 1951, **82**, 1125) and Pailer, Schneglberger, and Reifschneider (*Monatsh.*, 1952, **83**, 513) have described the synthesis by two methods of racemic *C*-noremetine, which lacks the *C*-ethyl group of emetine.

Experimental

Ethyl N-3 : 4-*Dimethoxyphenethylmalonamate* (I; R = CO_2Et).—(*a*) A stirred solution of 3 : 4-dimethoxyphenethylamine (46·5 g.) in anhydrous ether (250 ml.) was treated dropwise with a solution of ethoxycarbonylacetyl chloride (19·5 g., 0·5 equiv.) in anhydrous ether (50 ml.). After 12 hr., water (100 ml.) was added, the aqueous layer was separated, and the ethereal layer was extracted with hydrochloric acid (10 ml. of 2N). The combined aqueous layers were saturated with ammonium sulphate and extracted successively with ether (4 × 200 ml.) and ethyl acetate (3 × 200 ml.); evaporation of the combined extracts yielded *ethyl* N-3 : 4-*dimethoxyphenethylmalonamate* (35·9 g., 93·5%), which after distillation at 110° (bath)/10^{-5} mm. crystallised from anhydrous ether as colourless needles, m. p. 63—64° (Found: C, 60·6; H, 7·25; N, 5·05. $C_{15}H_{21}O_5N$ requires C, 60·9; H, 7·2; N, 4·75%).

(*b*) (With Arthur Morgan.) 3 : 4-Dimethoxyphenethylamine (4·23 g.) was heated with ethyl malonate (11·2 g.) for 4½ hr. at 125°. Excess of ethyl malonate was removed by distillation at 10 mm., and the residue was distilled in a high vacuum. A colourless oil distilled at

175—190°/2 × 10^{-4} mm. and solidified on cooling. Crystallisation from ether gave colourless needles, m. p. 52—53° (4·83 g., 70%), sufficiently pure for cyclisation to the dihydro*iso*quinoline.

Ethyl 3 : 4-*Dihydro*-6 : 7-*dimethoxy*-1-iso*quinolylacetate* (II; R = CO_2Et).—A boiling solution of the foregoing compound (15·75 g.) in pure anhydrous toluene (300 ml.) was treated with phosphoric oxide (30 g.). The mixture was agitated, and the solid material occasionally broken up by means of a spatula. Further portions (2 × 30 g.) of phosphoric oxide were added after 10 and 25 min., and heating under reflux was continued for a total of 45 min. The mixture was well cooled whilst water (500 ml.) was added in portions. The aqueous layer was separated and the toluene layer extracted twice with hydrochloric acid (2 × 30 ml. of 2N). The combined aqueous solutions were washed twice with ether, made alkaline with a large excess of concentrated aqueous potassium carbonate, and extracted with ether (5 × 200 ml.). Evaporation of the dried extract left the crude *dihydro*iso*quinoline* as a clear reddish-brown gum (11·12 g., 75%), which crystallised from ether or acetone–light petroleum as pale yellow rhombic plates (9·8 g.), m. p. 84—85° raised to 85·5—86·5° by distillation at 130° (bath)/0·4 mm. and crystallisation from ether. For analysis it was dried at 56° for 1½ hr. over phosphoric oxide in a vacuum (Found: C, 64·9; H, 7·05; N, 5·20. $C_{15}H_{19}O_4N$ requires C, 64·95; H, 6·95; N, 5·05%). The *picrate* separated from ethanol as bright yellow rods, m. p. 165—167° (decomp.), raised by repeated crystallisation from ethyl acetate and ethanol to 168—169·5° (decomp.); it was dried at 100° for 1½ hr. over phosphoric oxide in a vacuum (Found: C, 50·0; H, 4·3; N, 10·9. $C_{21}H_{22}O_{11}N_4$ requires C, 49·8; H, 4·4; N, 11·0%). When crystallised from ethyl acetate, the picrate melted consistently at 161—163° (decomp.) and was converted into the higher-melting form on crystallisation from ethanol.

Cyclisation of the malonamate by means of phosphoryl chloride in boiling toluene was much less satisfactory than the above method.

Ethyl 1 : 2 : 3 : 4-*Tetrahydro*-6 : 7-*dimethoxy*-1-iso*quinolylacetate* (III).—A solution of the dihydro*iso*quinoline (21·54 g.) in acetic acid (200 ml.) was shaken with hydrogen and platinic oxide (0·2 g.); absorption of hydrogen (1·0 mol.) ceased after 2 hr. The filtered solution was evaporated to dryness and the residual gum was dissolved in water, half saturated with ammonium sulphate, made just alkaline to phenolphthalein with potassium carbonate, and extracted with ethyl acetate (5 × 150 ml.). The dried extract was evaporated and the residual yellow gum (20·28 g.) was distilled at 160° (bath)/5 × 10^{-3} mm. The distillate, which crystallised, was recrystallised twice from ether to give pale yellow rhombs (16·7 g., 77%), m. p. 75·5—76·5°. Recrystallisation thrice more from ether gave the pure *base* as colourless prisms, m. p. 77—78°, which were dried at 56° for 1½ hr. over phosphoric oxide in a vacuum (Found: C, 64·6; H, 7·5; N, 5·3. $C_{15}H_{21}O_4N$ requires C, 64·5; H, 7·6; N, 5·0%). The *picrate* crystallised from ethanol as golden-yellow needles, m. p. 181—183° (Found: C, 49·8; H, 4·8. $C_{21}H_{24}O_{11}N_4$ requires C, 49·6; H, 4·8%).

Ethyl 1-*Piperidinobutane*-2-*carboxylate*.—(*a*) A mixture of ethyl α-ethylacrylate (3·2 g.) (Mannich and Ritsert, *Ber.*, 1925, **57**, 1117) and piperidine (2·1 g.) was kept at room temperature for 10 days. On distillation a small low-boiling fraction was removed, and the main fraction (3·28 g.) boiled at 107—109°/7 mm. It was dissolved in dilute hydrochloric acid, and the solution was extracted with ether. The product was reprecipitated by the addition of ammonia, extracted with ether and redistilled at 109—110°/8 mm., giving *ethyl* 1-*piperidinobutane*-2-*carboxylate* as a colourless oil (2·88 g.) from which no crystalline derivatives could be obtained (Found: C, 67·5; H, 10·6; N, 6·2. $C_{12}H_{23}O_2N$ requires C, 67·5; H, 10·9; N, 6·6%).

(*b*) Piperidine (0·7 g.) and ethyl α-formylbutyrate (1·2 g., 1 equiv.) (cf. Décombe, *loc. cit.*; Ingold, Perren, and Thorpe, *J.*, 1922, **121**, 1782) were mixed, considerable heat being developed. After 1 hr. the oil was taken up in ether, dried (Na_2SO_4) and distilled; ethyl 1-piperidinobut-1-ene-2-carboxylate (1·3 g., 75%) was collected as a pale yellow oil, b. p. 135°/4 mm. Its solution in ethanol (30 ml.) was shaken with hydrogen and platinic oxide (0·1 g.), absorption of hydrogen (1·1 mol.) ceasing after 4 hr. After removal of the catalyst and evaporation of the solvent, the product distilled at 108—110°/9 mm. as a colourless oil (1·2 g.).

2-(2-*Ethoxycarbonylbutyl*)-1-*ethoxycarbonylmethyl*-1 : 2 : 3 : 4-*tetrahydro*-6 : 7-*dimethoxy*iso*quinoline* (IV).—A solution of the tetrahydro*iso*quinoline (III) (3·94 g.) in anhydrous benzene (40 ml.) was heated with ethyl α-formylbutyrate (2·5 g., 1·2 equiv.) under a 15-cm. Vigreux column, so that slow distillation of benzene occurred; the volume was kept constant by the addition of dry benzene to the mixture. After 1¼ hr., when about 100 ml. of benzene had distilled, the mixture was evaporated on the steam-bath in a vacuum, and the residue was dissolved in acetic acid (30 ml.) and shaken with hydrogen and platinic oxide (0·2 g.); 1·02 mol. of hydrogen were absorbed in 1¾ hr. (Both the product and the unchanged ethyl α-formyl-

butyrate are reduced by this process.) After filtration, the solvent was evaporated under reduced pressure and the residue was taken up in N-hydrochloric acid (40 ml.) and washed with ether (3 × 50 ml.). The aqueous solution was treated with a large excess of solid potassium carbonate, and the product was extracted with ether (3 × 100 ml.). The extract, after being washed with water (10 ml.), dried, and evaporated yielded a yellow gum (4·56 g.). This was treated with ethyl α-formylbutyrate (2·0 g.) as before, and the crude product was hydrogenated in acetic acid solution, 0·41 mol. of hydrogen being absorbed. The basic material (5·3 g.) was isolated from the product as before, and was freed from unchanged secondary base by heating it with acetic anhydride (15 ml.) on the steam-bath for 1½ hr., basic material being then isolated in the usual way. The clear yellow gum (4·35 g., 75%) thus obtained was distilled twice at 120° (bath)/8 × 10^{-5} mm., giving an almost colourless gum (Found: C, 64·8; H, 8·4; N, 3·3. $C_{22}H_{33}O_6N$ requires C, 64·7; H, 8·15; N, 3·45%). The *diester* subsequently crystallised, and after recrystallisation thrice from light petroleum (b. p. 40—60°) formed colourless rods, m. p. 76—77°.

Heating together the tetrahydro*iso*quinoline (III) and ethyl α-ethylacrylate at 75—85° for 40 hr. failed to give the desired substance (IV). The product, after removal of neutral material and secondary base as above, distilled at 120° (bath)/2 × 10^{-5} mm. as a yellow gum (Found: C, 65·0; H, 7·55; N, 4·8%).

3-*Ethyl*-1 : 2 : 3 : 4 : 6 : 7-*hexahydro*-9 : 10-*dimethoxy*-2-*oxobenzo*[a]*quinolizine* (V).—The foregoing diester (10·4 g.) in anhydrous toluene (50 ml.) was added during 3 min. to a stirred suspension of freshly prepared sodium ethoxide (1·8 g.) in anhydrous toluene (60 ml.). The mixture was stirred and the alcohol formed in the reaction was removed by allowing slow distillation of a part of the toluene through a 7″ Vigreux column for 1 hr. After being boiled under reflux for a further hr., the solution was cooled in ice to precipitate the sodium salt of the product, the toluene was decanted, and the salt was hydrolysed by being heated with 2N-hydrochloric acid (150 ml.) for 7½ hr. at 100°. The cooled solution was washed twice with ether, basified with a large excess of solid potassium carbonate, and extracted with ether (5 × 75 ml.). Evaporation of the dried extract left a brownish solid (6·06 g., 82%), which crystallised from ether as pale yellow needles (5·12 g.), m. p. 108—109° after sintering at 107°; after recrystallisation from ether and sublimation at 120°/0·4 mm. the *ketone* (V) formed colourless needles, m. p. 109—109·5° (Found: C, 70·3; H, 7·8; N, 5·1. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 8·0; N, 4·9%). Evaporation of the ethereal mother-liquors from the crystallisation left a yellow gum which was twice distilled at 130° (bath)/5 × 10^{-4} mm. (Found: C, 69·3; H, 7·7; N, 4·9%). Gradual concentration of an ethereal solution of the distillate gave successive crops of the crystalline ketone.

Ethyl 1-*Methyl*-4-*piperidylacetate*.—Ethyl α-cyano-1-methyl-4-piperidylideneacetate (1·57 g.) (McElvain and Lyle, *J. Amer. Chem. Soc.*, 1950, **72**, 384) was hydrolysed by being heated under reflux with 2N-hydrochloric acid (20 ml.) for 8 hr. The solution was made alkaline to phenolphthalein and extracted thrice with ether, the aqueous solution being retained for further treatment (see below). The ethereal extract after drying and evaporation yielded an oil (0·675 g.), which distilled completely at 99—101°/6 mm. to give a colourless, unsaturated base, presumed to be 1-methyl-4-piperidylideneacetonitrile. A portion (0·37 g.) was dissolved in ethanol and shaken with hydrogen and palladised strontium carbonate (0·5 g.) until one mol. of hydrogen had been absorbed (1 hr.). Uptake of hydrogen continued beyond this point, but the hydrogenation was stopped, the catalyst was removed by filtration, and the solution was evaporated to dryness. The residue was dissolved in aqueous ethanol (8 ml. of 50%) containing potassium hydroxide (2 g.) and heated under reflux for 26 hr. The solution was acidified with hydrochloric acid and evaporated to dryness, and the residue was extracted thoroughly with absolute ethanol. The extract was evaporated to dryness, and the residue was again taken up in absolute ethanol (20 ml.) and filtered from traces of potassium chloride. The solution was mixed with concentrated sulphuric acid (0·5 ml.) and heated under reflux for 3 hr. After being concentrated to about 10 ml., the solution was poured into concentrated aqueous potassium carbonate, and the liberated amino-ester (0·39 g.) was isolated by ether-extraction. It distilled at 100° (bath)/15 mm. as a colourless oil, and yielded a *picrate*, m. p. 160—161°, as yellow needles from alcohol (Found: C, 46·2; H, 5·2; N, 13·8. $C_{16}H_{22}O_9N_4$ requires C, 46·4; H, 5·4; N, 13·5%).

The aqueous alkaline liquor from the original hydrolysis was acidified with hydrochloric acid and evaporated to dryness. The residue was extracted with glacial acetic acid (20 ml.), and the filtered extract, containing the acidic products of the hydrolysis, was boiled under reflux for 9 hr. The solvent was evaporated, and the residue was dissolved in water, made alkaline with potassium hydroxide, and extracted 4 times with ether, which removed only a trace of a

yellow oil. The aqueous solution was again acidified, evaporated to dryness, and extracted with glacial acetic acid, the extract on evaporation leaving crude 1-methyl-4-piperidylidene-acetic acid as a brown gum (0·47 g.). It was dissolved in aqueous acetic acid and shaken with hydrogen and platinic oxide (0·05 g.), 1·0 mol. of hydrogen being absorbed in 1½ hr. The product was esterified as described above, yielding a yellow oil (0·4 g.) which distilled at 100° (bath)/15 mm. and gave a picrate, m. p. 157—159°, identical with that obtained previously.

Ethyl 3-*Ethyl*-1 : 2 : 3 : 4 : 6 : 7-*hexahydro*-9 : 10-*dimethoxybenzo*[a]*quinolizin*-2-*ylacetate* (VI).—A mixture of the 2-oxoquinolizine (V) (1·74 g.), ethyl cyanoacetate (2 g.), glacial acetic acid (0·29 g.), ammonium acetate (0·105 g.), and benzene (1·5 ml.) was heated so that slow distillation of benzene occurred. Dry benzene was added to the mixture to keep the volume constant. After 2 hr. the benzene was evaporated, and the residue was dissolved in 3N-hydrochloric acid (50 ml.). The solution was extracted twice with ether to remove a red oil (0·336 g.) which was rejected, and it was then boiled under reflux for 24 hr., made alkaline with potassium carbonate, and extracted with ether (4 × 75 ml.). The extract on evaporation left a yellow gum (0·364 g.) which partly crystallised when seeded with the oxoquinolizine, and which also contained some unsaturated material; it was not examined further. The aqueous phase was acidified to Congo-red with hydrochloric acid and evaporated to dryness under reduced pressure, and the residue was extracted several times with glacial acetic acid (total, 125 ml.). The filtered extract was boiled under reflux for 14 hr. and evaporated under reduced pressure. The residue was dissolved in water, basified, and extracted with ether which removed a little yellow gum (25 mg.). The aqueous solution was acidified and evaporated, and the residue was extracted with absolute ethanol. The extract was freed from inorganic salts by evaporation and re-extraction with ethanol. Evaporation then left the amino-acid fraction as a pale yellow resin (1·82 g.), which was dissolved in glacial acetic acid (20 ml.) and hydrogenated over platinic oxide, absorption of hydrogen (58 ml., *ca.* 0·5 mol.) ceasing after ¾ hr. After removal of catalyst and solvent, the product was dissolved in ethanol (100 ml.) containing sulphuric acid (3 ml.). The solution was heated under reflux for 3 hr., concentrated to 20 ml., and poured into ether (300 ml.) and concentrated aqueous potassium carbonate (40 ml.). The ester was isolated from the ethereal layer as a dark red-brown gum (1·34 g.), which on distillation at 120° (bath)/2 × 10^{-5} mm. gave a yellow gum (0·911 g.), unaffected by being shaken in ethanol with hydrogen and platinic oxide. After two further distillations at 100—110° (bath)/4 × 10^{-5} mm. the ester was still not pure (Found: C, 63·9; H, 8·0; N, 3·9. Calc. for $C_{21}H_{31}O_4N$: C, 69·8; H, 8·7; N, 3·9%).

2-*Dicyanomethylene*-3-*ethyl*-1 : 2 : 3 : 4 : 6 : 7-*hexahydro*-9 : 10-*dimethoxybenzo*[a]*quinolizine* (IX).—The ketone (V) (1·8 g.), malononitrile (0·5 g.), ammonium acetate (0·2 g.), acetic acid (0·4 g.), and anhydrous benzene (5 ml.) were heated at 125° under a short column. Fresh benzene was added to replace that which distilled, and after 45 min. water no longer distilled with the benzene. Ether (50 ml.) was added to the cooled mixture, and dry hydrogen chloride was passed in; an amorphous, hygroscopic hydrochloride was precipitated. The solvent was decanted and the precipitate was dissolved in water and treated with alkali. The liberated yellow base crystallised on contact with ether, and had m. p. 153—154° (1·99 g., 95%). By crystallisation from ether (400 ml.) in a Soxhlet apparatus the condensation *product* formed fine yellow needles (1·7 g.), m. p. 157—158°, raised on further crystallisation to 159—159·5° (Found: C, 71·0; H, 6·8; N, 12·6. $C_{20}H_{23}O_2N_3$ requires C, 71·2; H, 6·9; N, 12·5%).

Condensation of the Ketone (V) *with* α-*Cyano*-N-3 : 4-*dimethoxyphenethylacetamide*.—The ketone (3·0 g.), α-cyano-*N*-3 : 4-dimethoxyphenethylacetamide (2·6 g.) (Child and Pyman, *J.*, 1931, 36), and dry ammonium acetate (1·0 g.) were heated in dry benzene (25 ml.) so that slow distillation of benzene occurred, the volume of the reaction mixture being kept constant by addition of fresh benzene at the same rate. After 4 hr. the benzene was distilled off and the residue dissolved in 2N-hydrochloric acid (30 ml.). The solution was thoroughly extracted with ether which removed α-cyano-*N*-dimethoxyphenethylacetamide (0·56 g.), then basified with a large excess of solid potassium carbonate, and again extracted with ether (7 × 70 ml.). The ethereal extract yielded a yellow gum (4·29 g.) which was dissolved in 9 : 1 benzene–light petroleum (200 ml.) and chromatographed on alumina. The chromatogram was developed with benzene containing a trace of ethanol, two clearly defined fractions passing through. The first (0·84 g.) gave on crystallisation from ether the unchanged ketone (0·6 g.), m. p. and mixed m. p. 107—108°. The second (2·14 g.) crystallised from ether to give crude 2-[α-*cyano*-α-(N-3 : 4-*dimethoxyphenethylcarbamyl*)*methylene*]-3-*ethyl*-1 : 2 : 3 : 4 : 6 : 7-*hexahydro*-9 : 10-*dimethoxybenzo*[a]*quinolizine* (X) (1·44 g.), m. p. 128—133°. Further elution of the column and further chromatography of the eluate gave an additional quantity (0·24 g.) of the desired product. Further purification of the product by crystallisation from ether in a Soxhlet apparatus gave

yellow needles, m. p. 147—147·5°, which were dried at 80° in a vacuum over phosphoric oxide (Found : C, 69·0; H, 7·0; N, 7·7. $C_{30}H_{37}O_5N_3$ requires C, 69·3; H, 7·2; N, 8·1%).

The product having been obtained crystalline by this procedure, it was possible to simplify subsequent preparations. Thus, the ketone (5 g.) yielded 6·76 g. of crude material from the ethereal extract, and this was dissolved in dry ether (100 ml.) and seeded with the pure product. The crystals (2·56 g.; m. p. 137—139°) which slowly separated were collected, and the mother-liquor was evaporated to dryness. The residue, mainly unchanged ketone, was again treated with cyanodimethoxyphenethylacetamide and by the same process yielded the crystalline product (2·71 g.; m. p. 133—135°). Recrystallisation of the combined products gave fairly pure material (4·8 g.; m. p. 141—143°) which was further purified as above.

Attempted Cyclisation of the Condensation Product (X).—A portion of the above product (0·1 g.) was cyclised with phosphoric oxide (2 g.) in toluene in the usual manner, and the basic product (88 mg.) was dissolved in benzene–light petroleum and passed through a column of alumina. A small first fraction was rejected, and the main eluate (51 mg.) was further chromatographed similarly and freed from solvent at 100° in a high vacuum for 3 hr. (Found : C, 70·3; H, 6·9; N, 8·1. Calc. for $C_{30}H_{35}O_4N_3$: C, 71·8; H, 7·0; N, 8·04%). The analytical results indicated that the product was contaminated with the original amide and, in an attempt to remove this by hydrolysis, the material (35 mg.) was heated under reflux for 5 hr. with constant-boiling hydrochloric acid. After cooling and removal of neutral products by ether-extraction, the basic material (20 mg.) was recovered as usual, and its solution in benzene–light petroleum (70 : 30) was passed through a column of alumina. Elution with benzene containing a little ethanol gave one main fraction (15 mg.) which partly crystallised; the crystals, m. p. 97·5—98·5°, were identified by mixed m. p. as 3 : 4-dihydro-6 : 7-dimethoxy-1-methyl*iso*quinoline (m. p. 102—103°).

2-[α-*Cyano*-α-(N-3 : 4-*dimethoxyphenethylcarbamyl*)*methyl*]-3-*ethyl*-1 : 2 : 3 : 4 : 6 : 7-*hexahydro*-9 : 10-*dimethoxybenzo*[a]*quinolizine* (XI).—A solution of the foregoing product (X) (0·61 g.) in absolute ethanol (150 ml.) was hydrogenated at atmospheric temperature and pressure over palladised strontium carbonate (6 g.), absorption of hydrogen (1·0 mol.) ceasing after 3 hr. After filtration, evaporation, and treatment with ether, the *product* (0·61 g.) crystallised (m. p. 165—169°); recrystallisation from ether (Soxhlet) and from ethanol gave colourless needles, m. p. 174—175° (Found : C, 68·8; H, 7·7; N, 8·4. $C_{30}H_{39}O_5N_3$ requires C, 69·05; H, 7·56; N, 8·1%).

(±) *Rubremetinium Bromide.*—(*a*) The ester (VI) (0·485 g.) and 3 : 4-dimethoxyphenethylamine (0·27 g.) were mixed and heated at 190° for 2 hr. A further portion (0·1 g.) of the amine was added and heating continued at 210° for 5 hr. The product, a dark resin, was freed from excess of amine and unchanged ester in a short-path still at 130—140° (bath)/4 × 10^{-5} mm. during several hr., and was then distilled at 200° (bath)/4 × 10^{-5} mm.; it then formed a yellow resin which could not be crystallised. A portion of the distilled amide (0·212 g.) was heated with purified toluene (5 ml.) and phosphoryl chloride (1 ml.) under reflux for 75 min. After being cooled, the toluene solution was extracted with water (15 ml.) and with 2N-hydrochloric acid (2 × 5 ml.). The combined acid extracts were basified with potassium hydroxide and extracted thrice with ether (total, 300 ml.), yielding after drying and evaporation a brownish gum (0·124 g.). Distillation gave fractions (i) b. p. 140—150° (bath)/4 × 10^{-5} mm. (57 mg.) and (ii) b. p. 180° (bath)/4 × 10^{-5} mm. (48 mg.). Fraction (ii) was shown to contain the desired product by its oxidation with mercuric acetate (*J.*, 1949, S 67) to (±)-rubremetinium bromide. Cyclisation of the amide with phosphoric oxide gave a similar result.

(*b*) A solution of the dimethoxyphenethylamide (XI) (2·53 g.) in purified *pseudo*cumene (50 ml.) was boiled under reflux for 1·5 hr., phosphoric oxide (24 g.) being added in 3 portions during the first hour. Water (100 ml.) was added to the cooled mixture, the acid aqueous layer was separated, and the *pseudo*cumene was extracted twice with dilute hydrochloric acid. The combined aqueous extracts were washed with ether, basified with excess of potassium hydroxide, and extracted with ethyl acetate (5 × 100 ml.). Evaporation of the extracts yielded a red gum (2·02 g.) which was treated with ether (2 × 100 ml.) to separate it into soluble (1·13 g.) and insoluble (0·89 g.) fractions. A portion (0·12 g.) of the latter was crystallised from ethanol, to give impure starting material (81 mg.), m. p. 166—169° (mixed m. p. 169—172°). The ether-insoluble fraction was therefore treated again with phosphoric oxide (3 × 4 g.) in *pseudo*cumene and gave a further 0·37 g. of ether-soluble base (total, 1·5 g.; 61%). The product was hydrolysed and decarboxylated by being boiled under reflux with 6N-sulphuric acid (100 ml.) for 24 hr. The solution was then made alkaline with sodium hydroxide and extracted with ether (5 × 100 ml.), the extracts yielding a clear yellow gum (0·95 g.). The more volatile material

(approx. 0·2 g.) was removed by short-path distillation at 100°/1·0 mm. for 1 hr. The material which did not distil was dissolved in water (30 ml.) containing acetic acid (1·1 ml.). Potassium acetate (0·2 g.) and mercuric acetate (4·2 g.) were added and the solution was heated under reflux for 1 hr. The solution was cooled and the precipitated mercurous acetate was removed and washed with water. Additional mercuric acetate (2·0 g.) was added to the filtrate which was heated for a further 4 hr. Rubremetinium chloride (0·207 g.) was isolated from the mixture as described previously (*J.*, 1949, S 67). After crystallising twice from dilute hydrochloric acid, it was converted into the bromide and this was crystallised from very dilute hydrobromic acid to give pure (±)-*rubremetinium bromide*, m. p. 185—190° after much previous sintering. Before analysis, the material was dried at 100° in a vacuum [Found: C, 62·3; H, 5·9; N, 5·6. $C_{29}H_{33}O_4N_2Br$ requires C, 62·9; H, 6·0; N, 5·1%. Pyman (*J.*, 1914, **105**, 1591) found for (+)-rubremetinium bromide: C, 62·2; H, 6·5%].

Our sincere thanks are offered to Dr. G. D. Meakins, Chemistry Department, University of Manchester, for the infra-red absorption measurements, and to Mr. E. S. Morton for the microanalysis of (±)-rubremetinium bromide. We are also grateful to Imperial Chemical Industries Limited for grants for the purchase of chemicals.

UNITED COLLEGE, UNIVERSITY OF ST. ANDREWS. [*Received, April 10th*, 1953.]

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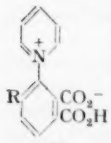
500. *Displacements of Anionoid Substituents in Phthalic Anhydrides by Pyridine and β-Picoline.*

By M. P. BALFE, M. DOUGHTY, and J. KENYON.

Pyridine and β-picoline react with 3-nitro- and 3 : 6-dichloro-phthalic anhydrides to yield betaines (I). Similar replacements of groups adjacent to electron-attracting substituents by pyridine and other electrophilic molecules are well-known. The reactions now described have two interesting features: First, the carboxyanhydro-group both activates the replacement of the *o*-substituent and, after ring-opening, assumes the negative charge which is required for the formation of the betaine (when a nitro-group is displaced, a betaine is the only product which can be isolated, because the nitrite ion is not sufficiently stable to permit the isolation of a pyridinium nitrite). Secondly, the carboxy-anhydride ring system is particularly effective in activating the *o*-anionoid group. Other evidence is reviewed which shows that electron-attraction by the $\overset{+}{C}\longrightarrow O$ dipole is particularly strong when the dipole is held in a ring system coplanar with the nucleus from which a group is to be displaced, which may be because the planar configuration is favourable to polar contributions in the resonance hybrid of the reacting molecule.

WHEN a solution of 3-nitrophthalic anhydride in pyridine is heated, brown nitrous fumes are evolved for about 12 hr., after which the hydrate of 1-(2 : 3-dicarboxyphenyl)-pyridinium betaine (I; R = H) can be isolated from the solution (in 50% yield on the weight of anhydride), the nitro-group having been displaced by pyridine.



(I)

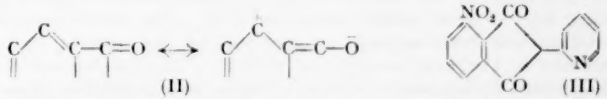
There are many recorded examples of anionoid displacement of groups—including nitro-groups—adjacent to electron-attracting substituents in aromatic nuclei, and fairly numerous examples of replacement of such groups by pyridine: there is one example of the displacement of nitro-groups by pyridine—its reaction with 1 : 8-dinitroanthraquinone (*Chem. Zentr.*, 1903, ii, 1099).

If the displaced group is stable as an anion, then a pyridinium salt is obtained; if the cation contains a group which can assume a negative charge the salt is the salt of a betaine (see, *e.g.*, Zincke, *J. pr. Chem.*, 1910, **82**, 19). The nitro-group is not sufficiently stable as an anion to permit the isolation of a pyridinium nitrite. The reaction product from the displacement of a nitro-group by pyridine can therefore only be identified when the aromatic nucleus contains a group such as carboxyl or hydroxyl capable of assuming a negative charge, thus enabling a betaine to be isolated.

The novel feature of the reaction with 3-nitrophthalic anhydride is that the anhydro-group first activates the displacement of the *o*-nitro-group and then (after ring opening) assumes the negative charge which produces the insoluble betaine. Similarly the carboxy-anhydride group can activate the displacement of *o*-chlorine: 3 : 6-dichlorophthalic anhydride reacts with pyridine and the resulting dibetaine can be isolated from the products of reaction. The anhydro-group does not, of course, activate the *m*-position: 4-chloro- and 4-nitro-phthalic anhydrides do not react with pyridine.

Although many groups retain their electron-attraction in pyridine solution yet they apparently do not facilitate the displacement of an *o*-anionoid group by pyridine: 2-chloro- and 2-nitro-benzoic anhydride, 2-ethyl 1-hydrogen 3-nitrophthalate, 2-ethyl 1-hydrogen 3 : 6-dichlorophthalate, and 5-hydroxy-2-nitrobenzaldehyde do not react with pyridine. In the recorded examples of the entry of pyridine into an aromatic nucleus, the displaced group is usually halogen and two adjacent (2 : 6-)nitro-groups are required to activate it (Borsche and Rautscheff, *Annalen*, 1911, **379**, 152; Zincke *et al.*, *Annalen*, 1904, **330**, 361; **333**, 296). A nitro-group can, however, be activated by one adjacent nitro-group: thus *o*-dinitrobenzene reacts with pyridine evolving brown fumes (betaine formation is impossible and a reaction product cannot be isolated), and 2 : 3-dinitrobenzoic acid reacts similarly, yielding a betaine of the probable structure (I; R = NO_2). Thus it appears that the $\overset{+}{C}\!\!\rightarrow\!\!O$ dipole of the cyclic carboxy-anhydride group is as powerful in *o*-activation as the nitro-group and much more powerful than the $\overset{+}{C}\!\!\rightarrow\!\!O$ dipoles in the linear anhydride group and the aldehyde-group.

There is a considerable body of evidence that an anionoid group attached to an aromatic nucleus is particularly easy to replace when there is in the *o*-position a carbonyl group which forms part of a ring system; *e.g.*, in substituted phthalic anhydrides (Pratt and Perkins, *J. Amer. Chem. Soc.*, 1918, **40**, 198, 219; Marriott and Robinson, *J.*, 1939, **134**; and the present experiments), anthraquinones (Barnett, " Anthracene and Anthraquinone," Baillière, Tindall, and Cox, London, 1928, p. 199), 1-chloroxanthone (Dhar, *J.*, 1917, **117**, 1068), and 1-chloro-4-nitroacridone (Nisbet and Goodlet, *J.*, 1932, 2772). In all these examples the activating carbonyl group is held in a ring system which is coplanar with the aromatic nucleus from which a group is displaced; presumably the coplanarity increases the activation because it favours the contribution of the structure (II) in the resonance hybrid.



(II) (III)

β-Picoline reacts with 3-nitrophthalic anhydride, yielding the β-methyl betaine analogous to (I). α-Picoline yields 4-nitro-2-2′-pyridylindane-1 : 3-dione (III) in accordance with the known reactivity of its methyl group. Quinoline, and nicotinic and α-picolinic acid, reacted with 3-nitrophthalic anhydride with the evolution of brown fumes but no definite products could be isolated. Hot triethylamine does not dissolve 3-nitrophthalic anhydride or react with it in solvents (dilution with dioxan prevents the reaction of pyridine with the anhydride).

Experimental

Interaction of 3-Nitrophthalic Anhydride and Pyridine: Formation of 1-(2 : 3-Dicarboxyphenyl)pyridinium Betaine Hydrate.—A mixture of 3-nitrophthalic anhydride (10 g.) and pyridine (30 c.c.; b. p. range 0·6°) contained in a flask fitted with a narrow air-condenser (30″) was heated in an oil-bath at 105—110°. The initially clear yellow solution became deep brown within 15 min. and brown fumes of oxides of nitrogen appeared. After an hour a yellowish-brown crystalline cake was being deposited on the sides of the flask: with continued heating the deposit blackened and increased in amount and after 12 hr. evolution of brown fumes ceased. The cooled product was filtered off and the crystalline material washed with light petroleum, crushed, and dried (6·8 g.); after two crystallisations from aqueous alcohol (33%) (norite), it formed slightly yellow prisms (1·9 g.). It darkens at 120° and decomposes to a

black mass at 270—280° [Found : C, 60·1; H, 4·3; N, 5·0%; *M* (by titration with NaOH), 261·5. $C_{13}H_9O_4N,H_2O$ requires C, 59·8; H, 4·2; N, 5·35%; *M*, 261·2].

The following salts were readily prepared from the betaine : 1-(2 : 3-*dicarboxyphenyl*)-*pyridinium chloride*, yellow prisms (from aqueous alcohol), m. p. 185—190° (decomp.) (Found : N, 4·45; Cl, 11·8. $C_{13}H_9O_4N,HCl,H_2O$ requires N, 4·7; Cl, 12·0%), *acetate*, prisms (from acetic acid), m. p. 199—200° (Found : C, 59·6; H, 4·4; N, 5·0. $C_{15}H_{13}O_6N$ requires C, 59·4; H, 4·3; N, 4·6%), and *picrate*, yellow needles (from methanol), m. p. 184—185° (Found : C, 49·5; H, 2·6; N, 11·9. $C_{19}H_{12}O_{10}N_4$ requires C, 50·0; H, 2·65; N, 12·2%).

Non-interaction of 3-*Nitrophthalic Anhydride and Pyridine in Dioxan.*—A solution of the anhydride (5 g.) in dry dioxan (20 c.c.) and pyridine (10 c.c.) was kept at 100° for 12 hr.; the solution darkened but slightly, evolved no brown fumes and, by evaporation, yielded unchanged anhydride, m. p. 160—163°.

Interaction of 3-*Nitrophthalic Anhydride and Quinoline.*—A solution of the anhydride (5 g.) in freshly distilled dry quinoline (20 c.c.) after being kept at 105—106° for 30 min. began to evolve nitrous fumes and continued doing so for 24 hr. The main product was a black tar which yielded no crystalline material.

Interaction of 3-*Nitrophthalic Anhydride and* β-*Picoline : Formation of* 1-(2 : 3-*Dicarboxyphenyl*)*picolinium Betaine Hydrate.*—A solution of the anhydride (10 g.) in purified β-picoline (15 c.c.) was slowly heated to 110° : brown fumes were evolved and a rather vigorous reaction ensued during which dark brown crystals began to separate. After 12 hr. at 110° the mixture was filtered and the solid (2·35 g.) washed with light petroleum. After two crystallisations from aqueous alcohol (norite) the *betaine monohydrate* was obtained as buff-coloured clusters of prisms which decomposed with blackening at 215—217° [Found : C, 61·0; H, 4·9%; *M* (by titration with NaOH), 277. $C_{14}H_{11}O_4N,H_2O$ requires C, 61·1; H, 4·8%; *M*, 275·3].

Interaction of 3 : 6-*Dichlorophthalic Anhydride and Pyridine : Formation of* 2 : 3-*Dicarboxyphenylene*-1 : 4-*bispyridinium Dibetaine.*—A solution of the anhydride (7·5 g.) in pyridine (15 c.c.) was kept at 110° : within 20 min. crystals began to separate and after 2 hr. the product became a brown sludge. This was diluted with light petroleum and filtered, the separated solid being washed with light petroleum until free from pyridine. This crude material (8·8 g.) after two crystallisations from aqueous acetone yielded the *pentahydrate* of the dibetaine as long colourless needles which darkened at 180° but did not melt below 330° [Found : C, 53·0; H, 5·6; N, 6·45; H_2O (loss at 105°), 21·0. $C_{18}H_{12}O_4N_2,5H_2O$ requires C, 52·7; H, 5·4; N, 6·8; H_2O, 20·9%].

Interaction of 2 : 3-*Dinitrobenzoic Acid and Pyridine : Isolation of* 1-(6-*Carboxy*-2-*nitrophenyl*)*pyridinium Picrate.*—A solution of 2 : 3-dinitrobenzoic acid (m. p. 201—202°; 1·5 g.) in pyridine (10 c.c.), kept at 110° for 2 hr., slowly darkened and evolved brown fumes: the solution was then heated under gentle reflux for 8 hr. The crystalline precipitate (0·36 g.) after two crystallisations from aqueous acetone yielded the betaine, as buff-coloured stout rods which darkened at 170° and decomposed at 225°. This betaine was characterised as the derived *picrate* (formed in aqueous methanol), bright yellow needles (from methanol), m. p. 191° (Found : C, 45·4; H, 2·2; N, 14·8. $C_{18}H_{11}O_{11}N_5$ requires C, 45·7; H, 2·3; N, 14·4%).

The following pairs of compounds when kept at 110—115° for 6—8 hr. readily evolved oxides of nitrogen; the other products of the reactions were generally dark amorphous solids or tars from which no crystalline material could be isolated : (i) *o*-dinitrobenzene and pyridine; (ii) *o*-dinitrobenzene and picolinic acid. Tetrachlorophthalic anhydride and pyridine yielded non-crystalline products.

Compounds which are Stable to Hot Pyridine.—When solutions, in an excess of pyridine, of each of the following compounds were kept at 110° for 8—20 hr., the compounds were recovered unchanged: 3-nitrophthalic acid, m. p. 215—216°; 2-ethyl 1-hydrogen 3-nitrophthalate, m. p. 156—157°; 4-nitrophthalic anhydride, m. p. 117—119°; 3-nitrophthalimide, m. p. 214—215°; 3-iodophthalimide, m. p. 237—239°; 5-hydroxy-2-nitrobenzaldehyde, m. p. 166—167°; *o*-nitrobenzoic anhydride, m. p. 134—135°; *o*-chlorobenzoic anhydride, m. p. 79—81°; *p*-dinitrobenzene, m. p. 171—172°; 4-chlorophthalic anhydride, m. p. 95—96°.

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BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, April 16th*, 1953.]

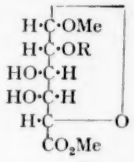
501. *Synthesis of* 2-O-*Methyl- and* 3 : 4-*Di*-O-*methyl*-D-*galacturonic Acid.**

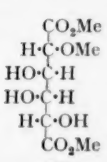
By R. A. Edington and Elizabeth E. Percival.

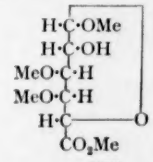
Crystalline methyl (methyl 3 : 4-*O*-*iso*propylidene-α-D-galactosid)uronate (B) has been synthesised from D-galactose. Methylation of (B) gave methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactosid)uronate (C) which was characterised by isolation of a crystalline amide, by oxidation to dimethyl 2-*O*-methyl-D-galactarate and by formation of the known crystalline diamide thereof. Hydrolysis of (C) gave 2-*O*-methylgalacturonic acid which on appropriate treatment gave the same diamide.

The crystalline 2-toluene-*p*-sulphonyl derivative of (B) was prepared, and removal of the *iso*propylidene residue followed by methylation and reductive fission of the toluene-*p*-sulphonyl group gave methyl 3 : 4-di-*O*-methyl-D-galactosiduronic acid. The methyl ester and its corresponding amide and methylamide were also obtained.

Apart from their intrinsic interest the methyl ethers of galacturonic acid are of great importance in the structural studies of the polysaccharides occurring in plant gums and pectins and in certain bacterial polysaccharides. Methylation followed by hydrolysis of these polysaccharides has led to a number of partially methylated galacturonic acid derivatives (Luckett and Smith, *J.*, 1940, 1106, 1506; Hirst, Hough, and Jones, *J.*, 1949, 3145; Brown, Hirst, and Jones, *J.*, 1949, 1761; Hough and Jones, *J.*, 1950, 1199). In addition G. A. Adams *et al.* (*Canad. J. Res.*, 1950, **28**, *B*, 753; *Canad. J. Chem.*, 1951, **29**, 109) isolated a monomethyl galacturonic acid from the hydrolysis products of the unmethylated polysaccharide from the hemicelluloses of wheat. The present work is concerned with the synthesis of 2-*O*-methyl- and 3 : 4-di-*O*-methyl-galacturonic acid. Methyl (methyl 2-*O*-methyl-α-D-galactopyranosid)uronate (I; R = Me) has been synthesised


(I)


(II)


(III)

previously by Jones and Stacey (*J.*, 1947, 1340) from 1 : 2 : 3 : 4-tetra-*O*-acetyl-6-*O*-tritylgalactose, which on removal of the trityl residue and oxidation gave 1 : 2 : 3 : 4-tetra-*O*-acetylgalacturonic acid. Hydrolysis of the acetyl groups and treatment with 1% methanolic hydrogen chloride then gave methyl (methyl α-D-galactosid)uronate (I; R = H). The hydroxyl groups at $C_{(3)}$ and $C_{(4)}$ were blocked by an *iso*propylidene residue and methylation followed by hydrolysis gave methyl (methyl 2-*O*-methyl-D-galactosid)-uronate in approximately 75% overall yield. The present synthesis differs in the earlier stages and gives a 20% overall yield. 1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galactose was oxidised with permanganate, giving crystalline potassium 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galacturonate monohydrate. This was converted into the crystalline free acid monohydrate which when boiled in dry methanol with cation-exchange resins furnished crystalline methyl (methyl α-D-galactosid)uronate. Although different conditions for the substitution and for the removal of the *iso*propylidene residue have been used, the subsequent stages were the same as those employed by Jones and Stacey (*loc. cit.*). In the present experiments the syrupy methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactopyranosid)uronate was characterised by the isolation of a crystalline amide and by oxidation to dimethyl 2-*O*-methylgalactarate (II). This, on appropriate treatment, gave the known crystalline diamide. Hydrolysis of the *iso*propylidene and glycosidic and

* For nomenclature, see *J.*, 1952, 5108, especially rules 9, 20, 26, 27, and 28.

ester methoxyl groups from methyl (methyl 2-*O*-methyl-3 : 4-*O*-*iso*propylidene-α-D-galactopyranosid)uronate and oxidation of the resulting 2-*O*-methyl-D-galacturonic acid with bromine water gave the same dimethyl ester which after treatment with methanolic ammonia furnished the above-mentioned crystalline diamide.

Crystalline methyl (methyl 3 : 4-di-*O*-methyl-α-D-galactopyranosid)uronate (III) has been synthesised by blocking position 2 in crystalline methyl (methyl 3 : 4-*O*-*iso*propylidenegalactosid)uronate with a toluene-*p*-sulphonyl group. Hydrolysis of the *iso*propylidene residue followed by methylation gave crystalline methyl (methyl 3 : 4-di-*O*-methyl-2-*O*-toluene-*p*-sulphonylgalactosid)uronate. Reductive fission of the toluene-*p*-sulphonyl group with sodium amalgam and separation from the toluenesulphinic acid and metallic ions by adsorption on ion-exchange resins followed by preferential elution led to the isolation of crystalline methyl 3 : 4-di-*O*-methylgalactosiduronic acid. Treatment with methanolic hydrogen chloride furnished the methyl ester (III) as long needles, and appropriate treatment gave a crystalline amide and methylamide. It was converted into crystalline methyl (methyl-2 : 3 : 4-tri-*O*-methyl-α-D-galactopyranosid)uronate. Hydrolysis of (III) followed by oxidation gave crystalline diethyl 3 : 4-di-*O*-methylgalactarate. The corresponding crystalline dimethyl ester and diamide were isolated.

Experimental

Methyl (Methyl α-D-Galactopyranosid)uronate.—D-Galactose (80·0 g.) was converted into 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galactose by the method described by Ohle and Berend (*Ber.*, 1925, **58**, 2585). The syrupy product, when distilled in a high vacuum, had b. p. 130—170°/0·03 mm., n_D^{25} 1·4657 (yield, 55·3 g., 76%), $[\alpha]_D^{19}$ −51° (*c*, 1·2 in H_2O) [Found : $COMe_2$, 44·9. Calc. for $C_{12}H_{20}O_6$: $COMe_2$, 44·6%).

Oxidation of this syrup (55·0 g.) by potassium permanganate as described by Ohle and Berend (*loc. cit.*) gave potassium 1 : 2-3 : 4-di-*O*-*iso*propylidene-D-galacturonate monohydrate (48 g., 70%), m. p. 200° (decomp.), $[\alpha]_D^{21}$ −70° (*c*, 2·0 in H_2O) (Found : C, 43·3; H, 5·5; $COMe_2$, 36·0. Calc. for $C_{12}H_{17}O_7K,H_2O$: C, 43·6; H, 5·8; $COMe_2$, 35·2%). 1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galacturonic acid was obtained by treatment of this (16 g.) with cation-exchange resins (Amberlite I.R. 100-H) (24 g.) in distilled water (200 c.c.) for 6 hr. The resins were removed by filtration and the filtrate was passed through a column (250 × 18 mm.) of the same resin. Removal of part of the water gave the acid as colourless crystals (12·7 g., 91%), m. p. 158°, $[\alpha]_D^{17}$ −79° (*c*, 0·9 in $CHCl_3$) (Niemann and Link, *J. Biol. Chem.*, 1934, **104**, 197, record m. p. 157°, $[\alpha]_D$ −84°) (Found : C, 50·1; H, 6·9; $COMe_2$, 40·0; CO_2, 16·1. Calc. for $C_{12}H_{18}O_7,H_2O$: C, 49·3; H, 6·9; $COMe_2$, 39·8; CO_2, 15·1%).

1 : 2-3 : 4-Di-*O*-*iso*propylidene-D-galacturonic acid monohydrate (13·9 g.) was boiled for 24 hr. with dry methanol (200 c.c.) containing cation-exchange resins (Amberlite I.R. 100-H). Removal of the resins and evaporation gave a colourless syrup which on trituration with ethanol partly crystallised (3·6 g., 32%). Repeated treatment of the mother-liquor with methanol and resins brought the total yield of crystalline methyl (methyl α-D-galactosid)uronate to 7·48 g. (66%), m. p. 145°, $[\alpha]_D^{16}$ +121° (*c*, 1·0 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 147°, and Niemann and Link, *loc. cit.*, $[\alpha]_D$ +121°) (Found : C, 39·9; H, 6·6; OMe, 26·5. Calc. for $C_8H_{14}O_7,H_2O$: C, 40·0; H, 6·7; OMe, 25·8%).

Methyl (Methyl 3 : 4-O-isoPropylidene-α-D-galactosid)uronate.—Methyl (methyl α-D-galactosid)uronate monohydrate (3·6 g.) was shaken for 120 hr. with dry acetone (250 c.c.) containing acetaldehyde (2 drops) and anhydrous copper sulphate (30 g.). A white solid was obtained which on recrystallisation from light petroleum (b. p. 60—80°) gave colourless needles (3·62 g., 94%), m. p. 113—114°, $[\alpha]_D$ +117° (*c*, 1·2 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 107°, $[\alpha]_D^{20}$ +118°) (Found : C, 50·8; H, 6·7; OMe, 23·2. Calc. for $C_{11}H_{18}O_7$: C, 50·4; H, 6·9; Me, 23·7%).

Methyl (Methyl 2-O-Methyl-α-D-galactopyranosid)uronate.—The foregoing *iso*propylidene compound (3·8 g.) was methylated thrice with methyl iodide and silver oxide, and the product distilled (b. p. 120—130°/0·1 mm.) as a colourless syrup (*A*) (2·70 g., 72%), n_D^{17} 1·4622, $[\alpha]_D^{16}$ +103° (*c*, 0·7 in H_2O), +114° (*c*, 0·8 in MeOH) (Found : C, 52·8; H, 7·4; OMe, 33·3. Calc. for $C_{12}H_{20}O_7$: C, 52·2; H, 7·3; OMe, 33·7%). This was characterised by conversion into the crystalline *amide* by treatment with methanolic ammonia. After recrystallisation from ethanol–light petroleum (b. p. 60—80°) the crystals had m. p. 123—124°, $[\alpha]_D^{19}$ +70° (*c*, 1·1 in H_2O)

(Found : C, 49·9; H, 7·1; N, 5·0; OMe, 23·7. $C_{11}H_{19}O_6N$ requires C, 50·6; H, 7·3; N, 5·4; OMe, 23·8%).

Mild hydrolysis of the *iso*propylidene residue was carried out in three ways : (1) A solution of the syrup (*A*) (2·48 g.) in methanol (50 c.c.) containing water (0·20 c.c.) was shaken with dry cation-exchange resins (Amberlite I.R. 100-H) (1·5 g.) for 6 days. Filtration and removal of the solvent gave methyl (methyl 2-*O*-methyl-α-D-galactopyranosid)uronate as a colourless syrup (2·18 g., 98%), n_D^{17} 1·4680, $[\alpha]_D$ +105° (*c*, 0·7 in MeOH), +113° (*c*, 0·8 in H_2O) (Jones and Stacey, *loc. cit.*, record n_D 1·4732, $[\alpha]_D^{20}$ +80°) (Found : C, 45·3; H, 6·9; OMe, 39·7. Calc. for $C_9H_{16}O_7$: C, 45·8; H, 6·8; OMe, 39·4%). (2) Similar treatment of (*A*) for 48 hr. at 50° gave a syrup (98%), $[\alpha]_D$ +97° (*c*, 0·7 in MeOH). (3) Treatment of (*A*) with 0·5% methanolic hydrogen chloride at 70° for 70 min. gave a syrup (98%), n_D^{17} 1·4679, $[\alpha]_D^{17}$ +4·0° (*c*, 1·7 in H_2O) (Brown, Hirst, and Jones, *J.*, 1949, 1761, record $[\alpha]_D$ +21° in H_2O). The derived amide, after recrystallisation from ethanol–ether, had m. p. 174—175°, $[\alpha]_D^{15}$ +60° (*c*, 1·3 in H_2O) (Jones and Stacey, *loc. cit.*, record m. p. 174°, $[\alpha]_D^{15}$ +55° in EtOH) (Found : C, 43·8; H, 6·6; N, 6·8; OMe, 28·4. Calc. for $C_8H_{15}O_6N$: C, 43·4; H, 6·8; N, 6·3; OMe, 28·1%).

Characterisation of Methyl (*Methyl* 2-O-*Methyl*-3 : 4-O-iso*propylidene-* and 2-O-*Methyl*-α-D-*galactosid*)*uronate*.—A portion of the syrup (*A*) (0·12 g.) was oxidised with nitric acid (*d* 1·3) by raising the temperature from 40° to 80° during 15 min., and then kept at 80° for 10 min. After removal of the nitric acid by distillation under diminished pressure, with frequent additions of water, the product was esterified by boiling it for 6 hr. with methanolic hydrogen chloride (4%). The resulting ester, dimethyl 2-*O*-methyl-D-galactarate, gave on distillation a syrup (0·07 g.), b. p. 160—180°/0·1 mm., from which a crystalline diamide, m. p. 205° (decomp.), was obtained on treatment with methanolic ammonia for 48 hr. at 0° (Jones and Stacey, *loc. cit.*, record m. p. 200°; Brown, Hirst, and Jones, *loc. cit.*, give m. p. 195° for this product from methylated *Cholla* gum; Hough and Jones, *loc. cit.*, give m. p. 207° for the same derivative from methylated gum from *Sterculia setigera*).

The syrup (*A*) (0·3 g.) was hydrolysed with 0·2N-sulphuric acid at 100° until the rotation was constant ($[\alpha]_D$ +36°; 48 hr.). Neutralisation was effected with barium carbonate and 2-*O*-methyl-D-galacturonic acid was obtained as a colourless syrup ($[\alpha]_D^{18}$ +42°), after elution through a column (160 × 12 mm.) of cation-exchange resin (Amberlite I.R. 120-H). Oxidation with bromine, followed by ester formation, furnished dimethyl 2-*O*-methyl-D-galactarate which had n_D^{15} 1·4640, $[\alpha]_D^{18}$ +34° (*c*, 3·0 in H_2O). The diamide prepared as above had m. p. 205° (decomp.) (Found : C, 37·8; H, 6·2; N, 11·6; OMe, 14·9. Calc. for $C_7H_{14}O_6N_2$: C, 37·8; H, 6·4; N, 12·6; OMe, 14·0%).

Methyl (*Methyl* 3 : 4-O-iso*Propylidene*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate*.—The above-mentioned *iso*propylidene derivative, m. p. 113—114° (0·931 g.), was dissolved in dry pyridine (20 c.c.) and kept with "Drierite" (12 g.) at 0° for 20 hr. Toluene-*p*-sulphonyl chloride (1·6 g.) in dry pyridine (10 c.c.) was added in small portions during several hours, the mixture being kept at 0°. The solution was then set aside for 24 hr. at 0°, for 24 hr. at 15°, and for 72 hr. at 30° (unless these conditions are observed the yield is much diminished). The mixture was cooled to 0°, the "Drierite" removed by filtration, and water (100 c.c.) cautiously added with constant cooling. *Methyl* (*methyl* 3 : 4-O-iso*propylidene*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate* (*B*) was deposited as colourless needles (1·02 g.), m. p. 157—158°, $[\alpha]_D^{20}$ +122° (*c*, 1·1 in MeOH), +117° (*c*, 2·2 in $CHCl_3$) (Found : C, 52·0; H, 5·5; S, 8·1; OMe, 14·6. $C_{18}H_{24}O_9S$ requires C, 51·9; H, 5·8; S, 7·8; OMe, 14·9%). After removal of the crystals, extraction of the aqueous filtrate with chloroform and removal of the solvent gave a further yield (0·23 g.) of crystals (total yield, 1·255 g., 85%).

Methyl (*Methyl* 3 : 4-*Di*-O-*methyl*-2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate*.—The crystals (*B*) (1·345 g.), dissolved in 1% methanolic hydrogen chloride (130 c.c.), were kept at 30° for 30 hr. After neutralisation with silver carbonate *methyl* (*methyl* 2-O-*toluene*-p-*sulphonyl*-α-D-*galactosid*)*uronate* (*C*) (1·18 g., 97%) was obtained. After recrystallisation from aqueous methanol it had m. p. 71°, $[\alpha]_D^{18}$ +61° (*c*, 1·1 in $CHCl_3$) (Found : C, 45·8; H, 5·7; S, 8·4; OMe, 15·2. $C_{15}H_{20}O_9S,H_2O$ requires C, 45·7; H, 5·6; S, 8·1; OMe, 15·7%). Methanolic anhydrous ammonia quantitatively converted the ester into the *amide* which crystallised on removal of the solvent. The amide after recrystallisation from methanol had m. p. 94—95°, $[\alpha]_D^{18}$ +67° (*c*, 0·5 in $CHCl_3$) (Found : C, 45·1; H, 5·6; N, 3·5; S, 8·1; OMe, 8·2. $C_{14}H_{19}O_8NS,H_2O$ requires C, 44·3; H, 5·6; N, 3·7; S, 8·4; OMe, 8·2%).

The product (*C*) (1·18 g.) was methylated four times with methyl iodide and silver oxide. The resultant *dimethyl ether* (1·21 g., 96%) was dissolved in warm ethanol and crystallisation induced by the addition of water. After recrystallisation from aqueous methanol it had m. p.

83°, n_D^{20} 1·4900, $[\alpha]_D^{17}$ +82° (*c*, 1·1 in $CHCl_3$), +88° (*c*, 2·4 in EtOH) (Found: C, 50·2; H, 5·8; OMe, 29·5; S, 8·1. $C_{17}H_{24}O_9S$ requires C, 50·5; H, 6·0; OMe, 30·7; S, 7·9%).

Methyl 3 : 4-*Di*-O-*methyl*-α-D-*galactosiduronic Acid*.—Anion-exchange resin (Amberlite I.R.A. 400-OH) was packed into four short glass tubes (60 × 10 mm.) which were arranged alternately with three similar tubes containing cation-exchange resin (Amberlite I.R. 120-H) to form a column, and the whole washed with distilled water (300 c.c.), with ethanol (200 c.c.), and with methanol (200 c.c.).

Methyl (methyl 3 : 4-di-*O*-methyl-2-*O*-toluene-*p*-sulphonyl-α-D-galactosid)uronate (1·2 g.), dissolved in methanol (20 c.c.), was stirred at room temperature with 0·25N-aqueous sodium hydroxide (12 c.c.) during 30 min.; thereafter sodium amalgam (4%; 15 g.) was added during 6 hr. with continuous stirring. The mixture was stirred for a further 18 hr. and then the solids were removed by filtration and washed with methanol. After treatment with solid carbon dioxide the combined filtrates were evaporated to dryness and a white solid was obtained which was repeatedly extracted with dry methanol under reflux. The cooled methanolic extracts (200 c.c.) were passed through a column, prepared as described above, 3—4 c.c. of eluate being collected during a minute, and, after complete elution, the eluate was recycled through the column which was finally washed with methanol (100 c.c.). Removal of the solvent from the combined eluate and washings gave a syrup (0·03 g.) which was discarded. The column was dismantled and the portions containing the anion-exchange resin reassembled and eluted by slow passage (60 hr.) of 2% formic acid in methanol (500 c.c.). Removal of solvent from the eluate, under reduced pressure, gave *methyl* 3 : 4-*di*-O-*methyl*-α-D-*galactosiduronic acid* as a colourless syrup (0·613 g., 87%) which crystallised spontaneously. Recrystallised from ethanol–light petroleum (b. p. 60—80°) it had m. p. 154—155°, $[\alpha]_D^{15}$ +158° (*c*, 1·3 in $CHCl_3$), +156° (*c*, 1·3 in MeOH), +163° (*c*, 1·3 in H_2O) (Found: C, 46·4; H, 7·0; OMe, 38·4. $C_9H_{16}O_7$ requires C, 45·8; H, 6·8; OMe, 39·4%).

Methyl (*Methyl* 3 : 4-*Di*-O-*methyl*-α-D-*galactosid*)*uronate*.—Methyl 3 : 4-di-*O*-methyl-α-D-galactosiduronic acid (0·375 g.), dissolved in methanolic hydrogen chloride (1%; 32 c.c.), was kept at 30° for 48 hr. The solution was neutralised with silver carbonate, and the filtrate after evaporation to dryness at 40°/15 mm. furnished a crystalline ester. Recrystallisation from light petroleum (b. p. 60—80°) gave needles of *methyl* (*methyl* 3 : 4-*di*-O-*methyl*-α-D-*galactosid*)-*uronate* (0·378 g., 95%), m. p. 113—114°, $[\alpha]_D^{16}$ +165° (*c*, 0·4 in $CHCl_3$) (Found: C, 48·0; H, 7·1; OMe, 49·8. $C_{10}H_{18}O_7$ requires C, 48·0; H, 7·25; OMe, 49·6%). The crystalline amide and *methylamide* were prepared by treating the ester, in the usual manner, with methanolic ammonia, and with methanolic methylamine respectively. The amide, after trituration with ethanol, had m. p. 130—131°, $[\alpha]_D^{17}$ +108° (*c*, 1·1 in EtOH). The methylamide, obtained as prisms on recrystallisation from acetone, had m. p. 205°, $[\alpha]_D^{15}$ +116° (*c*, 0·6 in H_2O) (Found: C, 48·5; H, 7·5; N, 5·8; OMe, 38·8. $C_{10}H_{19}O_6N$ requires C, 48·2; H, 7·7; N, 5·6; OMe, 37·4%).

The ester (0·018 g.) was methylated twice with methyl iodide and silver oxide, and crystalline methyl (methyl 2 : 3 : 4-tri-*O*-methyl-α-D-galactopyranosid)uronate (0·019 g.) was obtained. It had m. p. 71—72° (after sublimation *in vacuo*) alone and admixed with an authentic specimen.

Diethyl 3 : 4-*Di*-O-*methylgalactarate*.—The foregoing dimethyl ether ester (0·294 g.) was hydrolysed at 100° with sulphuric acid (20 c.c., 0·2N), the rotations observed being $[\alpha]_D$ +160° (0 hr.), +118° (3·5 hr.), +112° (6·5 hr.), +100° (24 hr.), +90° (31 hr.), +84° (48 hr., const.). The solution was neutralised with barium carbonate and filtered through a well-washed bed of charcoal–"Filter Cel," and barium ions were removed by passage of the filtrate through a column (300 × 10 mm.) of Amberlite (I.R. 120-H) ion-exchange resin. The clear eluate was concentrated to a colourless syrup, n_D^{11} 1·4615, $[\alpha]_D^{16}$ +37° (*c*, 1·2 in EtOH), +93° (*c*, 1·3 in H_2O). The syrup (0·22 g.) in water (15 c.c.) was oxidised with bromine (2 c.c.) at 40°, the rotations observed being $[\alpha]_D$ +93° (0 hr.), 80° (1 day), 60° (3 days), 23° (5 days), 15° (8 days, constant). After removal of the water and hydrobromic acid under diminished pressure with frequent addition of ethanol the syrupy residue was heated in hydrochloric acid (10 c.c.; 0·2N) at 100° for 50 hr. by which time the rotation had fallen to +8°. Further treatment with bromine (2 c.c.) for 3 days at 40° gave a solution with $[\alpha]_D$ ±0°. Removal of the water and hydrobromic acid as above gave crystalline *diethyl* 3 : 4-*di*-O-*methylgalactarate*. Recrystallisation from aqueous acetone gave flat plates, m. p. 148—149°, $[\alpha]_D$ ±0° [Found: C, 49·4; H, 7·4; OR (as OMe), 42·2. $C_{12}H_{22}O_8$ requires C, 49·0; H, 7·5; OR (as OMe), 42·2%]. Treatment with methanolic hydrogen chloride (1·5%) at 60° for 16 hr. gave a crystalline product. Recrystallisation from acetone–light petroleum (b. p. 60—80°) furnished *dimethyl* 3 : 4-*di*-O-*methylgalactarate* as needles, m. p. 172—173°, $[\alpha]_D$ ±0° (Found: 44·8; H, 6·7. $C_{10}H_{18}O_8$ requires

C, 45·1; H, 6·8%). The derived *diamide*, after recrystallisation from methanol, had m. p. 230° (decomp.), $[\alpha]_D$ ±0° (Found: N, 11·9. $C_8H_{16}O_6N_2$ requires N, 11·9%).

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502. *The Configurations of the Isomeric Forms of* 1 : 3-*Dimethylcyclopentane.*

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The configurations of the two stereoisomers of 1 : 3-dimethyl*cyclo*pentane have been established by synthesis. The previous tentative assignments must be reversed.

THE current assignment of configurations to the two geometrical isomers of 1 : 3-dimethyl*cyclo*pentane appears to have originated from the work of Glasgow (*J. Res. Nat. Bur. Stand.*, 1940, **24**, 509) who isolated one isomer from a Mid-Continent petroleum naphtha. The close similarity of the physical properties of the compound with an optically active, and therefore *trans*-, isomer prepared by Zelinsky and Rudsky (*Ber.*, 1896, **29**, 403; Zelinsky, *ibid.*, 1902, **35**, 2677) led Glasgow to conclude that his isomer was the *trans*-compound. When Rossini and his co-workers (Streiff, Zimmermann, Soule, Butt, Sedlak, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1948, **41**, 323) prepared both isomers it became apparent that this assignment was suspect owing to the very similar properties of the *cis*- and the *trans*-form.

Our present work shows conclusively that the current assignment of the *cis*- and *trans*-configuration to the 1 : 3-dimethy*cyclo*pentanes should be reversed as was necessary with the 1 : 3-dimethyl*cyclo*hexanes (Mousseron and Granger, *Bull. Soc. chim.*, 1938, **5**, 1618; Pitzer and Beckett, *J. Amer. Chem. Soc.*, 1947, **69**, 977; Beckett, Pitzer, and Spitzer, *ibid.*, 1947, **69**, 2488; Haggis and Owen, *J.*, 1953, 408).

An optically active *trans*-form and an inactive *cis*-form of 1 : 3-dimethyl*cyclo*pentane were synthesised by Mousseron and Granger (*Compt. rend.*, 1942, **215**, 161; Mousseron, *Bull. Soc. chim.*, 1946, **13**, 218) but the physical properties of these compounds differ so considerably from those of the A.P.I. materials that their results only indicate the probability of the *trans*-isomer's being the higher boiling. Birch and Oldham (*Nature*, 1947, **160**, 368) prepared a small quantity of a 1 : 3-dimethyl*cyclo*pentane and tentatively suggested the revision of the assignment of the configurations. Their synthesis, from *cis-cyclo*pentane-1 : 3-dicarboxylic acid, has now been considerably improved, and in addition two optically active hydrocarbons have been prepared from the *trans*-acid.

The conversion of *cis-cyclo*pentane-1 : 3-dicarboxylic acid, readily obtained by oxidation of norbornylene (*bicyclo*[2 : 2 : 1]hept-2-ene) (Birch, Oldham, and Johnson, *J.*, 1947, 818), into the corresponding hydrocarbon involved four steps. The acid was first converted into the ethyl ester, which, after fractionation under reduced pressure, was reduced to the corresponding diol with lithium aluminium hydride. Previously this reduction had been carried out by the Bouveault–Blanc method and by catalytic hydrogenation in the presence of copper chromite. While the Bouveault–Blanc product and its toluene-*p*-sulphonate possessed physical properties closely agreeing with those of the material obtained by use of lithium aluminium hydride, the glycol obtained by catalytic hydrogenation was, from its physical properties, obviously impure. The conversion of the ester into the glycol by lithium aluminium hydride, however, proceeded smoothly and gave an excellent yield of a product, the toluene-*p*-sulphonate of which gave a material of constant melting point after only two crystallisations. Proof that no detectable rearrangement had taken place during the reduction was afforded by reconversion of the glycol into the original acid by

oxidation with permanganate. This is in agreement with the demonstration by Noyce and Denney (*J. Amer. Chem. Soc.*, 1950, **72**, 5743) that this method of reduction of an ester does not affect the stereochemistry of the α-carbon atom. Reduction of the toluene-*p*-sulphonate in ether with lithium aluminium hydride by Strating and Backer's method (*Rec. Trav. chim.*, 1950, **69**, 638), gave a good yield of the corresponding hydrocarbon which was purified by fractionation and percolation through silica-gel. It boiled at the same temperature as, and had physical properties similar to, those of the material tentatively designated by Rossini and his co-workers as the *trans*-isomer. The identity of the two was confirmed by spectroscopic analysis, a direct comparison between the two materials being made. This definitely established that the isomer hitherto regarded as *trans* is in fact *cis*.

The purity of this hydrocarbon, as determined by its melting point, indicated the presence of 5·5—7·5% of an impurity shown by spectroscopic analysis to be the *trans*-isomer. The presence of this in a product derived from carefully purified *cis*-toluene-*p*-sulphonate was unexpected. As discussed above, the glycol must have been the *cis*-isomer and the purity of the toluene-*p*-sulphonate, indicated by its constant melting point, was confirmed by the fact that the addition of 7% of (+)-*trans*-toluene-*p*-sulphonate lowered the melting point from 108·5—109° to 104·5—107°; one crystallisation raised it to 107·5—108·5°. Reduction of the (+)- and (−)-*trans*-toluene-*p*-sulphonates similarly gave small amounts of the *cis*-isomer, *i.e.*, some isomerisation took place at this stage. The extent of isomerisation appears to be limited, and it is probable that by varying the conditions of reduction it could be appreciably reduced although this could not be confirmed experimentally. As an alternative to the reduction of the toluene-*p*-sulphonate with lithium aluminium hydride the Raney nickel desulphurisation of the cyclic sulphide,* formed by heating the toluene-*p*-sulphonate with sodium sulphide and necessarily having a *cis*-structure, was considered. It was not, however, investigated because of the difficulty in preparing enough material for determination of purity from the freezing point which in our equipment requires a minimum of 35 ml. Furthermore, isomerisation seemed more likely by this method. It is difficult from the physical properties reported by Haggis and Owen (*loc. cit.*) for their isomeric dimethyl*cyclo*hexanes to judge whether, in fact, these contained isomeric hydrocarbons, but from the figures given it would certainly appear that this could be so.

While the presence of *trans*-isomer in the amount found in the *cis*-hydrocarbon does not seriously affect the conclusions with regard to the configuration of the 1 : 3-dimethyl*cyclo*pentanes, any possible doubt would be eliminated by the synthesis of the other (*trans*-) isomer in optically active forms. Both Zelinsky and Mousseron in their syntheses employed optically active compounds derived in the first place from a naturally occurring product. With a source of *cis-cyclo*pentane-1 : 3-dicarboxylic acid available it was more convenient to start with this which Pospischill (*Ber.*, 1898, **31**, 1950) had shown could be isomerised to the (±)-*trans*-acid by hydrochloric acid at 180°. Separation of the resultant mixed acids by treatment with acetyl chloride, followed by extraction with ether and resolution of the *trans-form* with the aid of brucine, was carried out as described by Perkin and Scarborough (*J.*, 1921, **119**, 1400). This *trans*-acid obtained from the mixture of *trans*-acid and *cis*-anhydride melted at 89—92°. This melting point is appreciably higher than that reported by other workers for the pure acid. Thus Pospischill (*loc. cit.*) gives 87—88·5°, Semmler and Bartelt (*Ber.*, 1908, **41**, 385) 86°, Perkin and Scarborough (*loc. cit.*) 85—86°, while Ingold and Mohrhenn (*J.*, 1935, 949) obtained an acid from carbon tetrachloride melting at 83—85°, raised however to 89° on desiccation over phosphoric oxide. Accordingly the acid was treated a few times with carbon tetrachloride as described by Pospischill (*loc. cit.*) but little change in melting point was observed. Crystallisation from a mixture of carbon tetrachloride and benzene raised the melting point to a constant value of 95·5—96·5°. Addition of 1% of the *cis*-acid produced a slight depression, and addition of 5% lowered the melting point to 93·4—95·5°. From this it would appear that 95·5—96·5° is the true melting point of the pure *trans*-acid.

Resolution of the (±)-*trans*-acid showed that the acids obtained by Perkin and Scar-

* To be described in a future communication.

borough after three crystallisations of the brucine salts were not optically pure and that the amount of optically pure material which could be obtained from the available *trans*-acid would be insufficient for the subsequent stages of the synthesis. Accordingly the synthesis was continued with incompletely resolved materials. The best samples of acids, obtained after many crystallisations of the brucine salts, had $[\alpha]_D^{15}$ +21·3°, and $[\alpha]_D^{15}$ −22·6°, compared with $[\alpha]_D^{15}$ +5·8° and $[\alpha]_D^{15}$ −5·3° quoted by Perkin and Scarborough (*loc. cit.*). The partly purified (+)- and (−)-acids ($[\alpha]_D^{15}$ +13·6°, −20·2°) were converted by the route already described into the corresponding hydrocarbons with the exception that, instead of the lithium aluminium hydride reduction being carried out on the esters, the free acids were reduced (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548).

The two glycols and the two hydrocarbons derived from them were optically active. Their physical properties, and in particular the infra-red absorption spectra of the hydrocarbons, corresponded with those of the A.P.I. *cis*-material. Both forms contained some of the *cis*-form, in an amount estimated by refractive index and spectroscopic analysis as *ca.* 17 and 8% for the (−)- and the (+)-forms respectively. The conversion of the *trans*-acid into optically active hydrocarbons leaves no doubt as to the *trans*-configuration of the latter.

Physical properties of 1 : 3-*dimethyl*cyclo*pentanes*.

	A.P.I.*		Present work		
	"cis"	*"trans"*	*cis*	(−)-*trans*	(+)-*trans*
F. p.	−133·90°	−133·690°	(M. p.) −135·30°	—	—
d^{20}	0·74880	0·74479	0·7450	0·7481	0·7485
d^{25}	0·74435	0·74025	—	0·7437	0·7442
n_D^{20}	1·41074	1·40894	1·40904	1·41043	1·41060
n_D^{25}	1·40813	1·40633	—	1·40778	1·40799
B. p.	91·725°	90·773°	90·92°	91·6°	91·6°

* American Petroleum Institute Research Project 44, Selected Values of the Properties of Hydrocarbons, Table 6A, 1949.

Experimental.

M. p.s are corrected.

Diethyl cis-cyclo*Pentane*-1 : 3-*dicarboxylate*.—*cis-cyclo*Pentane-1 : 3-dicarboxylic acid (2528 g.) was esterified with ethanol (4068 ml.) in a continuous esterification apparatus (*Org. Synth.*, Coll. Vol. I, 1944, p. 261), carbon tetrachloride (1774 ml.) being used as entrainer and sulphosalicyclic acid (40 g.) as catalyst; the diethyl ester (2750 g.), fractionated through a 25-plate column, boiled at 149°/23 mm. and had n_D^{20} 1·4481. It set to a glass on cooling (Found: C, 61·55; H, 8·7. Calc. for $C_{11}H_{18}O_4$: C, 61·7; H, 8·5%).

cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The above ester (414 g., 1·93 moles), diluted with ether (1 l.), was slowly added to a stirred solution of lithium aluminium hydride (90 g., 2·37 moles) in ether (2 l.) during 2 hr., the temperature being kept at 30—35°. Stirring was continued for a further 2 hr. and the product containing excess of the hydride was then decomposed with water and dilute sulphuric acid. The aqueous layer was extracted continuously overnight with fresh ether. The combined ethereal solutions were dried (K_2CO_3) and evaporated, leaving a colourless viscous liquid which on distillation gave the *glycol* (244 g., 96·8%), b. p. 118°/0·5 mm., n_D^{20} 1·4855 (Found: C, 64·7; H, 11·2. $C_7H_{14}O_2$ requires C, 64·6; H, 10·8%).

The *phenylurethane*, prepared in the usual way, after crystallisation from ethanol–ligroin melted at 139—139·5° (Found: C, 68·6; H, 6·4; N, 7·5. $C_{21}H_{24}O_4N_2$ requires C, 68·5; H, 6·6; N, 7·6%).

Oxidation of cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The glycol (6·5 g.) was dissolved in water (100 ml.) and, while a stream of carbon dioxide was passed in, potassium permanganate (21 g.) in water (500 ml.) was added during 2 hr. Next morning the product was treated with sulphur dioxide, then concentrated, acidified, and extracted with ether. A solid product (3 g.) was obtained which after crystallisation from water melted at 118·5—119° alone or mixed with *cis-cyclo*pentane-1 : 3-dicarboxylic acid (Found: C, 52·8; H, 6·3. Calc. for $C_7H_{10}O_4$: C, 53·2; H, 6·4%). Extraction of the aqueous layer with ether in a continuous extractor gave 4 g. of an oil which was not further investigated.

Di-p-*toluenesulphonate of* cis-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—The glycol was converted into the *di*-p-*toluenesulphonate* as described in *Org. Synth.* (1940, **20**, 50). After two crystallisations from benzene–ethanol, a product (92% yield) consisting of needles, m. p.

108·5—109°, was obtained (Found : C, 57·7; H, 5·9; S, 14·5. $C_{21}H_{20}O_6S_2$ requires C, 57·5; H, 6·0; S, 14·6%).

cis-1 : 3-*Dimethyl*cyclo*pentane*.—The di-*p*-toluenesulphonate (360 g., 0·82 mole) was added in small portions to a stirred and cooled solution of lithium aluminium hydride (80 g., 2·11 moles) in ether (2000 ml.) at such a rate that the solvent refluxed gently. Addition was complete in 2 hr. and stirring continued for a further 6 hr. Excess of hydride was destroyed by the cautious addition of water (100 ml.), followed by dilute sulphuric acid (250 ml. in 1125 ml. of water). After being washed with aqueous sodium hydroxide to remove traces of thiocresol, the ether was distilled through a 50-plate column. The residual hydrocarbon after passing through silica-gel, with propanol as eluant, was fractionated through a low-hold-up column containing packing of the Bower and Cooke type (*Ind. Eng. Chem., Anal.*, **1943**, **15**, 290) equivalent to 30 theoretical plates. For the properties of the hydrocarbon (70·3 g., 87·4%) see the Table.

trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acid*.—*cis-cyclo*Pentane-1 : 3-dicarboxylic acid (12 g.) was heated with concentrated hydrochloric acid (15 ml.) at 180° for 6 hr. The product was washed out with water and evaporated to dryness on the steam-bath under reduced pressure. Treatment of the residue with acetyl chloride at room temperature for 24 hr., followed by removal of the volatile material in a desiccator over solid potassium hydroxide as recommended by Perkin and Scarborough (*loc. cit.*), yielded an approx. 1 : 1 mixture of *trans*-acid and *cis*-anhydride. Extraction four times with dry ether (20 ml.) dissolved the *trans*-acid, m. p. 81—85°. Repetition of this treatment of the acid with acetyl chloride, etc., gave crude *trans*-acid, m. p. 88—92°. It was dissolved in water (charcoal), then filtered, and the water evaporated off. A total of 130 g. of the *trans*-acid was prepared in this way. It was crystallised from benzene–carbon tetrachloride until a constant m. p. of 95·5—96·5° was reached.

(+)- *and* (−)-trans-cyclo*Pentane*-1 : 3-*dicarboxylic Acids*.—The (±)-*trans*-acid was converted into the brucine salt and resolved by fractional crystallisation from water as described by Perkin and Scarborough (*loc. cit.*). Approx. 3 l. of boiling water were required to dissolve the acid (123 g.) and the brucine (738 g.). The brucine salt of the (+)-acid was concentrated in the less soluble portion which crystallised out. Although a considerable number of crystallisations were carried out and both (+)- and (−)-acids were obtained possessing considerably higher optical activity than those previously described, complete optical purity was not achieved with either. The air-dried salt which gave a (+)-acid of highest activity had $[\alpha]_D^{15}$ +20·09° (*c*, 2 in 1 : 1 H_2O–EtOH, by vol.).

The acids, recovered from the brucine salts as described (*loc. cit.*), were recrystallised from benzene–carbon tetrachloride. The best samples had the following properties : (+)-acid, m. p. 79·5—80·5°, $[\alpha]_D^{15}$ +21·3°; (−)-acid, m. p. 85·0—85·7°, $[\alpha]_D^{15}$ −22·6° (*c*, 8 in H_2O). For conversion into the glycol, acids having rotations of $[\alpha]_D^{15}$ +13·6° (46·1 g.) and $[\alpha]_D^{15}$ −20·2° (34·5 g.) were used.

(−)- *and* (+)-trans-1 : 3-*Bishydroxymethyl*cyclo*pentane*.—Reduction of the acids with lithium hydride as described by Halford and Wassmann (*J. Org. Chem.*, 1952, **17**, 1276) gave a low yield of glycol and a considerable amount of unchanged acid. The molar ratio of acid to hydride was therefore increased to 1 : 4, 1800 ml. of ether being used per mole of the latter. The reaction mixture was decomposed with water and acidified with dilute sulphuric acid, and the aqueous portion continuously extracted with ether. Washing the combined ethereal layers with a little concentrated sodium hydroxide solution removed unchanged acid which was recovered from the alkaline extract by acidification and ether-extraction. This was similarly reduced and the glycol combined with the main product. After drying with potassium carbonate and removal of the ether, the glycol which remained was distilled under reduced pressure. It boiled at 117—118°/0·5 mm. and had n_D^{20} 1·4868. The glycol (76% yield) from the (+)-acid ($[\alpha]_D^{15}$ +13·6°) was a colourless viscous liquid, $[\alpha]_D^{15}$ −1·7°; the glycol (77% yield) from the (−)-acid ($[\alpha]_D^{15}$ −20·2°) had $[\alpha]_D^{15}$ +4·2° (*c*, 3·4 in EtOH).

The *di*-p-*toluenesulphonate* was prepared from the (−)-glycol, as for the *cis*-compound, in 84·4% yield. Crystallised once from ethanol it melted at 78—81° (Found : C, 57·3; H, 6·1; S, 14·5%). The corresponding *derivative* from the (+)-glycol, obtained similarly in 78·7% yield, melted after one crystallisation from ethanol at 69—75° (Found : C, 58·0; H, 6·1; S, 14·3%).

(−)- *and* (+)-trans-1 : 3-*Dimethyl*cyclo*pentane*.—The di-*p*-toluenesulphonate of (−)-*trans*-1 : 3-bishydroxymethyl*cyclo*pentane (80 g.) was slowly added to lithium aluminium hydride (34 g.) in ether (1000 ml.) at such a rate that the ether refluxed gently. When addition was complete, stirring was continued for a further 3 hr. after which the mixture was surrounded by a cooling-bath and decomposed first with water and then with dilute sulphuric acid. Washing,

drying ($CaCl_2$), and fractionation as for the *cis*-isomer gave a fraction (16·56 g., 92·5%) which was purified by percolation over silica gel to remove traces of ether and toluene (propanol as eluant). The properties of the final product are given in the Table; it had $[\alpha]_D^{15}$ −1·5°.

Similarly treated, the di-*p*-toluenesulphonate (57 g.) of (+)-*trans*-1 : 3-bishydroxymethyl-*cyclo*pentane yielded a hydrocarbon (11·8 g., 92·6%) which, purified as above, had the properties given in the Table, also $[\alpha]_D^{15}$ +2·3°.

We thank the Chairman of the Anglo-Iranian Oil Company Limited for permission to publish these results. We also acknowledge the help of Dr. H. Powell for the determination of the infra-red spectra of our hydrocarbons and of Messrs. J. F. Osborne and D. Ellis in the preparative work.

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503. *Amino-acids and Peptides. Part X.* The Nitrogenous Constituents of Some Marine Algae.*

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The chemical distribution of the nitrogen in samples of the brown seaweeds *Laminaria saccharina, Laminaria cloustoni, Ascophyllum nodosum,* and *Pelvetia canaliculata,* and in the red seaweed *Rhodymenia palmata,* has been determined. Peptides and proteins account for most of the organic nitrogen; there are small amounts of volatile bases, and in *L. cloustoni* and *R. palmata* appreciable quantities of free α-amino-acids (chiefly alanine, aspartic acid, and glutamic acid). The amino-acids obtained on hydrolysis of the *L. saccharina, A. nodosum, P. canaliculata, and R. palmata* samples have been identified by partition chromatography, and several have been determined quantitatively in the last two species. No amino-acid has been found which does not also occur in land plants. A preliminary investigation has been made of the complexity of the mixture of peptides and proteins in the *P. canaliculata* sample, by counter-current separation of their bromodinitrophenyl derivatives. The new reagent, 1-bromo-2-fluoro-3 : 5-dinitrobenzene, may prove useful for determining certain reactive groups in peptides, and, in special cases, their chain length.

THE amino-acids and peptides of marine algae are of interest not only because of the salt-water environment of the plants but also because of the suggestion by Haas and Hill (*Ann. Bot.*, 1933, **47**, 55) that the low intensity of the available light, or in some cases the periods of desiccation, might result in a modification of protein metabolism. These authors initiated investigations in this field by the isolation (*Biochem. J.*, 1931, **25**, 1472) of what appeared to be an octapeptide of glutamic acid from *Pelvetia canaliculata*, of the Phaeophyceae class (brown algae); subsequently, glycine, alanine, arginine, and histidine were also detected in peptides isolated from other samples of this species (Haas, Hill, and Russell-Wells, *ibid.*, 1938, **32**, 2129; Haas, *ibid.*, 1950, **46**, 503). From certain Rhodophyceae (red algae) of the sub-class Florideae, peptides of low molecular weight were obtained, containing alanine, phenylalanine, arginine, and aspartic acid (Haas, Hill, and Russell-Wells, *loc. cit.*; Haas and Hill, *ibid.*, 1933, **27**, 1801); glycine and histidine were found in addition in peptides from other samples of Florideae (Haas, *loc. cit.*). From the brown marine alga *Eisenia bicyclis*, Ohira (*J. Agric. Chem. Soc. Japan*, 1939, **15**, 370) isolated a peptide ("eisenine") which he suggested was L-5-oxopyrrolidine-1-carbonyl-L-glutaminyl-L-alanine (*ibid.*, 1940, **16**, 1, 293). More recently, Dekker, Stone, and Fruton (*J. Biol. Chem.*, 1949, **181**, 719) obtained a peptide considered to be L-5-oxopyrrolidine-1-carbonyl-L-glutaminyl-L-glutamine from *P. fastigiata*; they pointed out that the ring closure may have occurred during extraction.

Mazur and Clarke (*ibid.*, 1938, **123**, 729; 1942, **143**, 39) have investigated formic acid

* Part IX, *J.*, 1952, 3937.

extracts of certain Phaeophyceae, Rhodophyceae, and Chlorophyceae (green algae). They identified the amino-acids formed on hydrolysis, and determined several (see also Lugg, *Adv. Protein Chem.*, 1949, **5**, 247). Lugg also (*Biochem. J.*, 1943, **37**, 132) has examined hydrolysates of the green marine alga *Ulva lactuca*. Simultaneously with the publication of a preliminary note of our results (*J. Soc. Chem. Ind.*, 1952, 519), Ericson and Sjöström (*Acta Chem. Scand.*, 1952, **6**, 805) reported the identification of a wide range of amino-acids in the hydrolysates of brown algae of three different orders, *Sphacelaria arctica*, *Laminaria saccharina*, and *Fucus vesiculosus*. Excepting di-iodotyrosine, which Roche and Lafon (*Compt. rend.*, 1949, **229**, 481) detected in the base of the thallus of *L. saccharina* and *L. flexicaulis*, all the amino-acids reported to be present in hydrolysates of marine algae are also constituents of land-plant proteins.

Aliphatic amine salts occur in marine algae, methylamine and trimethylamine having been found (together with ammonium salts) by Kapeller-Adler and his co-workers (*Biochem. Z.*, 1930, **224**, 378; 1931, **243**, 292) in species of *Fucus* and in red and green algae. Haas and Hill (*Biochem. J.*, 1931, **25**, 1472) similarly found trimethylamine in *P. canaliculata*.

In the present investigation, we have examined samples of the brown algae *L. saccharina*, *L. cloustoni*, *Ascophyllum nodosum*, and *P. canaliculata*; the first two belong to the family Laminariaceae (order Laminariales) and the last two to the family Fucaceae (order Fucales). We have also examined a sample of the red alga *Rhodymenia palmata* (sub-class Florideae, order Rhodymeniales). The place and date of harvesting of each sample are shown in Table 1. Volatile bases were determined by aeration of a suspension in saturated aqueous

TABLE 1.

No.	Alga	Origin: When collected	Origin: Locality	Portion of plant
1	*Laminaria saccharina*	March, 1945	Eilean Coltair, Loch Melfort, Argyllshire	Frond
2	*L. saccharina*	Sept., 1945	" " "	"
3	*L. cloustoni*	July, 1948	Luing Island, Cullipool, Argyllshire	Frond
4				Stipe
5				Holdfast
6	*L. cloustoni*	Oct., 1948	" " "	Frond
7	*Pelvetia canaliculata*	June, 1948	Atlantic Bridge, Clachan Sound, Argyllshire	Whole plant
8	*P. canaliculata*	March, 1949	" " "	"
9	*Ascophyllum nodosum*	Dec., 1949	North Berwick, East Lothian	"
10	*Rhodymenia palmata*	Jan., 1952	" "	"

No.	Kjeldahl-N, %	Volatile base-N, %	Amide-N, %	Nitrate-N, %	Residual-N, %	Total org.-N, %	Residual-N, %, ×6·25	α-Amino-acid-N found after hydrolysis, %	Free α-amino-acid-N, %
1	2·39	0·05	0·22	0·86	1·81	2·08	11·3	1·30	—
2	0·71	0·01	0·09	0·01	0·59	0·69	3·7	0·53	—
3	1·58	0·03	0·25	0·02	1·27	1·55	7·9	—	0·20
4	1·61	0·05	0·17	0·19	1·24	1·46	7·8	—	0·23
5	2·42	0·07	0·25	0·31	1·86	2·18	11·6	—	0·22
6	1·55	0·05	0·28	0·06	1·15	1·48	7·2	1·08	—
7	0·88	0·01	0·11	0·03	0·72	0·84	4·5	0·63	—
8	1·73	0·01	0·32	0·04	1·36	1·69	8·5	1·10	0·06
9	1·58	0·03	0·29	0·03	1·22	1·54	7·6	1·00	—
10	3·91	0·01	0·48	0·13	3·28	3·77	20·5	2·80	0·25

All figures have been corrected for moisture.

potassium carbonate. Steam-distillation from sodium hydroxide gave the total of volatile base and amide-ammonia; reduction of the residue with Devarda's alloy reduced any nitrate present to ammonia, which was again distilled. The residue was digested by the Kjeldahl method, and the remaining nitrogen so determined. The chemical distribution of the nitrogen is shown in Table 1. Only very small amounts of ammonium and amine salts were present in these samples (column headed " volatile base "); examination of the conditions used in the work reported earlier (Channing and Young, *loc. cit.*) has shown that the figures reported then for " volatile-base nitrogen " will include much, but not all, of the amide-nitrogen. In contrast, Haas and Hill (*Ann. Bot.*, 1933, **47**, 55) found considerable amounts of ammonium salts in *L. digitata* (January) and *Fucus vesiculosus* (April)

samples. It should be noted that direct Kjeldahl determinations (Table 1) give unreliable values for the samples containing nitrate (compare column headed " total org.-N "). Dr. W. A. P. Black (personal communication) has found that when nitrate is added to algae samples a portion is reduced to ammonia during Kjeldahl digestion, whilst we have found that the Kjeldahl-nitrogen value of a known mixture of glycine with potassium nitrate corresponded to less than half of the glycine-nitrogen.

The total α-amino-acid-nitrogen obtained on hydrolysis of the algae samples was determined by titration of the carbon dioxide evolved in the reaction with ninhydrin (Van Slyke, MacFadyen, and Hamilton, *J. Biol. Chem.*, 1941, **141**, 671). Preliminary experiments with *Ascophyllum nodosum* showed that the optimum time of hydrolysis with boiling 6N-hydrochloric acid is *ca.* 72 hours, and this period was used for all the samples. It will be seen from Table 1 that in each case the α-amino-acid-nitrogen is lower than the " residual-nitrogen " determined as described above. Only small amounts of basic amino-acids have been found in the hydrolysates, and the most likely cause of this discrepancy is the destruction known to occur when proteins are hydrolysed in the presence of carbohydrate. The Table also gives an approximate figure for the percentage of peptide and protein in the dried seaweed; the high figure for *Rhodymenia palmata* is noteworthy.

Investigation of the bases distilled from a suspension of the *Pelvetia canaliculata* (March, 1949) sample in sodium hydroxide showed that the major constituent was ammonia (identified as toluene-*p*-sulphonamide). Extraction of the hydrochlorides with chloroform yielded trimethylamine hydrochloride (identified as the picrate). A trace of primary amine was detected in the chloroform-insoluble fraction, but the carbon content showed that an amine could not represent more than 5% of this fraction, which was chiefly ammonium chloride.

Preliminary work with A. Basu (unpublished) had shown that the holdfast of a *Laminaria cloustoni* sample (July, 1948) contained a significant amount of uncombined α-amino-acids. We now find that the frond and stipe of this plant also contain similar amounts, as does the *Rhodymenia palmata* sample (Table 1, last column). In contrast, the *Pelvetia canaliculata* sample contained little free α-amino-acid. Paper chromatography showed that in both *Laminaria cloustoni* and *Rhodymenia palmata* the main free α-amino-acids were alanine, aspartic acid, and glutamic acid; the latter species gave, in addition, spots corresponding to valine, the leucines, and proline. It is interesting that the first three amino-acids are those which in higher plants may be formed directly from the corresponding α-keto-acids, which are themselves known intermediates in plant metabolism.

Acid hydrolysates of the *L. saccharina* (Sept., 1945), *A. nodosum*, *P. canaliculata* (March, 1949), and *R. palmata* samples were then examined by partition chromatography in order to identify the constituent amino-acids. In the first two cases, a preliminary separation was effected by means of a column of powdered cellulose, with butanol–acetic acid–water as the developing solvent. The fractions so obtained were analysed by one-dimensional paper chromatography. In later work we effected the initial separation by partition of a " band " of the hydrolysate on paper (after removal of salts by electrodialysis). The position of the fractions so obtained was indicated by spraying the edges of the chromatogram with ninhydrin; the narrow strips were then cut out, and eluted, and the constituents identified by one-dimensional paper chromatography. By the use of a thick paper (Whatman No. 3), sufficient of each fraction could be provided for partition in several solvents.

The following amino-acids were identified in the hydrolysates of the *L. saccharina* and *A. nodosum* samples: glycine, alanine, valine, leucine, *iso*leucine, phenylalanine, serine, threonine, aspartic acid, glutamic acid, proline, lysine, and arginine. Acid hydrolysates of the *P. canaliculata* and *R. palmata* samples contained, in addition, methionine, tyrosine, and histidine. Ornithine was also found, but is likely to have been formed from arginine during electrodialysis (cf. Stein and Moore, *J. Biol. Chem.*, 1951, **190**, 103). In alkaline hydrolysates, tryptophan also was detected. We consider that these additional amino-acids may also have been present in the first two hydrolysates, the examination of which was less exhaustive. Our results agree with those of Ericson and Sjöström (*loc. cit.*), except that these authors found cystine but not tryptophan in their materials. All the amino-

acids reported are found in proteins from many other sources. Our results show little qualitative difference between the brown and the red samples.

Partition methods do not normally distinguish between enantiomorphs, and a preliminary experiment was performed to determine whether D-amino-acids were present in the hydrolysate of *P. canaliculata* (March, 1949). The volume of oxygen absorbed on treatment with a D-amino-acid oxidase preparation suggested that small amounts of D-amino-acids were present, but such quantities may well arise by racemisation during hydrolysis. This question deserves further investigation.

Certain of the main amino-acids in hydrolysates of *P. canaliculata* (March, 1949) and *R. palmata* have been determined quantitatively. The high accuracy of the isotope-dilution method did not appear to be required at this stage, and a convenient sub-micro-procedure was adopted. Partition on Whatman No. 3 paper separated a narrow band containing 0·4—2 mg. of the amino-acid to be determined, which was then eluted and estimated by the ninhydrin–carbon dioxide method. Known mixtures of amino-acids gave results between 98 and 107% of the theoretical (Table 4, p. 2489), and the analyses of the two seaweed samples are shown in Table 2; the separation of valine and tyrosine was incomplete and they were determined together. It will be seen that despite the difference in total α-amino-acid content, the brown and the red algae contain remarkably similar proportions of each of these amino-acids, except in the case of glutamic acid; it is interesting to recall the earlier isolation of a glutamyl-peptide from *P. canaliculata*. The aspartic acid and glutamic acid found in each case are together approximately equivalent to the amide-nitrogen (Table 1) and it seems that most of those carboxyl groups not in peptide linkage are present as amides. It must be emphasised that in these analyses no allowance has been made for the destruction of the amino-acids during hydrolysis.

TABLE 2.

	Amino-acid found,			
	N, % of total α-amino-acid-N		G. per 100 g. of dry sample	
Amino-acid	*P. canaliculata*	*R. palmata*	*P. canaliculata*	*R. palmata*
Alanine	9·7	10·8	0·65	1·85
Leucine	2·6	2·8	0·25	0·71
*iso*Leucine	2·9	2·6	0·28	0·66
Valine + tyrosine	5·4	5·1	0·60 *	1·46 *
Aspartic acid	7·5	8·6	0·75	2·20
Glutamic acid	18·0	8·4	1·98	2·37

* On the assumption that the nitrogen is equally distributed between valine and tyrosine.

TABLE 3.

	Bromodinitrophenyl-peptide fractions					
	EtOAc-soluble			BuOH-soluble		Residual H_2O-soluble
Amino-acids	A1	A2	A3	B1	B2	C
Aspartic acid	+	—	+	—	+	++
Glutamic acid	+++	++	+++	+	+++	+++
Glycine	±	—	+	—	—	+
Alanine	+	+	+	—	+	+
Serine	—	—	—	—	—	±
Valine	—	—	—	—	—	+
Leucine(s)	—	—	—	—	—	+
Phenylalanine	—	—	—	—	—	+
Histidine	±	—	±	—	—	±
Other basic amino-acids	—	—	—	—	—	±
N-Terminal amino-acids	—	Serine, glycine	Glycine	—	—	—

An attempt was made to examine the complexity of the peptides and proteins in the *P. canaliculata* (March, 1949) sample. Separation of such materials from the polysaccharide present is difficult, but preliminary experiments showed that the separation was facilitated by conversion into the *N*-dinitrophenyl derivatives (Sanger, *Biochem. J.*, 1945, **39**, 507).

There appeared also to be advantages in introducing, for example, a bromine atom into the nitrophenyl group; determination of the bromine in the derivative would then assay the reactive groups (amino, imino, phenolic-hydroxyl, and thiol), and in certain cases the chain length could then be deduced. With this object in mind, 1 : 3-dibromo-2-chloro-5-nitrobenzene was prepared, but the chlorine could not be replaced by fluorine under the usual conditions. However, 1-bromo-2-chloro-3 : 5-dinitrobenzene reacted smoothly with potassium fluoride to give 1-bromo-2-fluoro-3 : 5-dinitrobenzene as a crystalline solid, which coupled with amino-acids and peptides to give yellow or orange bromodinitrophenyl derivatives. Although, as will be seen, this method of chain-length determination could not be applied in the present work, it may be useful in other cases.

The *P. canaliculata* sample was extracted with cold 0·05N-sodium hydroxide, and the solution was saturated with carbon dioxide and then treated with 1-bromo-2-fluoro-3 : 5-dinitrobenzene in ethanol. The bromodinitrophenyl-peptides were precipitated with mercuric acetate and liberated by hydrogen sulphide; the aqueous solution was extracted first with ethyl acetate (to give fraction A), and then with butanol (fraction B), leaving an aqueous solution (fraction C) still containing peptide or protein derivatives. Evaporation of fractions A and B in the presence of aqueous ammonia gave residues which were subjected to counter-current partition between butanol and 5% aqueous ammonia, giving three fractions from A and two from B. From the small amount and unsatisfactory nature of these materials, it was clear that bromine determinations could give no reliable indication of the chain length, and each fraction was therefore hydrolysed and the amino-acids were identified by paper chromatography. Ether-extracts of the hydrolysates from A1, A2, and A3 contained the bromodinitrophenyl derivatives of the *N*-terminal amino-acids, and these were hydrolysed by ammonia, to yield the *N*-terminal amino-acids. Glycine and serine were so obtained from A2, and glycine alone from A3. The failure to detect *N*-terminal residues in the remaining fractions may have been due in part to the instability of their bromodinitrophenyl derivatives and in part to the small amount present. From Table 3 it will be seen that each fraction, except C, contained few amino-acids, and in every case glutamic acid was the major component. Fraction C contained many amino-acids and is likely to have been of considerably higher molecular weight.

Finally, it should be pointed out that the above conclusions apply to samples of algae collected and dried as indicated; whether or not significant changes occur after harvesting is a matter for further investigation.

Experimental

The dried, milled seaweed samples (see Table 1) were provided by the Institute of Seaweed Research, to whom we are indebted for the following details of preliminary treatment (cf. Black, *J. Soc. Chem. Ind.*, 1948, **67**, 165, 169, 172; 1949, **68**, 183; 1950, **69**, 161; *J. Marine Biol. Assoc.*, 1950, **29**, 45, 379): Drying was commenced within 3 hr. of collection as follows: *A. nodosum* and *R. palmata*, 24 hr. at 60—70°; others, 48 hr., *L. cloustoni* (July, 1948) at 60—70°, and *L. saccharina*, *L. cloustoni* (Oct., 1948), and *P. canaliculata* at 25—35°. The samples were then pulverised in a Christy and Norris No. 8 laboratory mill (64-mesh screen). We determined the moisture contents of the milled samples before use, by drying to constant weight at 60—62° *in vacuo* over phosphoric oxide.

Determination of the Chemical Distribution of the Nitrogen of the Algae Samples.—Ammonia-free air was bubbled for 2 hr. through an agitated suspension of the seaweed sample (0·6—1 g.) in saturated aqueous potassium carbonate (30 ml.). The volatilised bases were determined by absorption in aqueous boric acid and titration with standard hydrochloric acid (methyl red–bromocresol green indicator; Ma and Zuazaga, *Ind. Eng. Chem., Anal.*, 1942, **14**, 280).

A sample (0·3—0·5 g.) of the seaweed in water (10 ml.) was warmed for 5 min. with 40% aqueous sodium hydroxide (20 ml.), and the volatile bases (including the ammonia liberated from amide groups) were removed by steam-distillation, and absorbed and titrated as described above. Devarda's alloy (0·5 g.) was added to the residual alkaline solution to reduce nitrate (and nitrite if present) to ammonia, which after 1 hr. was steam-distilled, absorbed in boric acid, and titrated. The residual mixture was acidified with sulphuric acid and evaporated to small bulk, and its nitrogen content was determined by the Kjeldahl procedure of Campbell and Hanna (*J. Biol. Chem.*, 1937, **119**, 1).

Corresponding blank experiments were performed in each case. The procedures described gave satisfactory results with known synthetic mixtures.

Determination of the α-Amino-acid Nitrogen obtained by Acid Hydrolysis of the Algae.—Acid hydrolysis of the seaweed samples was by an excess of boiling 6N-hydrochloric acid under reflux. Initial experiments with *A. nodosum* indicated that hydrolysis for *ca.* 72 hr. gave the maximum yield of total α-amino-acid nitrogen, and this period was used in all subsequent hydrolyses. After removal of insoluble humin by filtration, the hydrolysate was evaporated below 50° *in vacuo* with repeated additions of water, to remove excess of hydrochloric acid. The residue was taken up in water, and the solution was filtered, if necessary, and made up to a known volume. The total α-amino-acid nitrogen was determined by the titrimetric ninhydrin–carbon dioxide method (Van Slyke, MacFadyen, and Hamilton, *loc. cit.*).

In several cases the insoluble humin was extracted with dilute aqueous ammonia, to dissolve any amino-acids precipitated with the humin. The α-amino-acid nitrogen content of these extracts was almost invariably less than 1% of that of the corresponding main hydrolysates.

Identification of the Volatile Bases from Pelvetia canaliculata (*March*, 1949).—The volatile bases obtained by steam-distillation of an alkaline suspension of the seaweed were treated with toluene-*p*-sulphonyl chloride; the only product identified was toluene-*p*-sulphonamide (m. p. and mixed m. p. with an authentic specimen, 136—137°). The volatile bases from a second portion of the seaweed were absorbed in dilute hydrochloric acid. The hydrochlorides obtained on evaporation were divided into (*a*) a chloroform-soluble portion in which trimethylamine was identified as its picrate (m. p. and mixed m. p. with an authentic specimen, 218°), and (*b*) a chloroform-insoluble portion consisting chiefly of ammonium chloride, in which a trace of primary amine was detected by the carbylamine reaction. Attempts to identify this amine by paper chromatography in butanol–acetic acid (Bremner and Kenten, *Biochem. J.*, 1951, **49**, 651) were unsuccessful. Fraction (*b*) contained 0·78% of carbon, corresponding to the presence of less than 5% of its weight of primary amine (calc. as $CH_3 \cdot NH_2$,HCl).

Determination and Identification of the Free α-Amino-acids.—The seaweed sample (*ca.* 1 g.) was shaken mechanically for 1 hr. with warm 75% (v/v) aqueous ethanol (3 × 30 ml.). After each treatment the extract was separated by centrifuging. The combined extracts were evaporated below 50° *in vacuo*, the residue was taken up in very dilute aqueous ammonia, the mixture was centrifuged, and the liquid was made up to a known volume for the estimation of the total α-amino-acid nitrogen (Table 1, last column).

The amino-acids present in the extracts were identified by one-dimensional paper chromatography in phenol (with ammonia vapour) and in butanol–acetic acid (see the section on paper chromatography). In all the cases examined, the main spots obtained corresponded to aspartic acid, glutamic acid, and alanine; the extract from *R. palmata* gave, in addition, spots corresponding to proline, valine, and leucine(s). Asparagine was not detected, but the possibility of the presence of glutamine could not be excluded as this overlaps alanine when chromatograms are run in phenol, and overlaps aspartic acid when butanol–acetic acid is used.

Qualitative Chromatographic Techniques.—(a) *Partition chromatography on cellulose columns.* The columns were prepared (from " Solka-Floc " powdered cellulose) and operated as described by Hough, Jones, and Wadman (*J.*, 1949, 2511), their automatic fraction-collector being used; we are indebted to Dr. J. K. N. Jones for guidance in the construction and operation of this apparatus. The columns were developed with butanol–acetic acid–water (40 : 11 : 19 vol.); this mixture is homogeneous, and gives R_F values similar to those given by the butanol–acetic acid mixture used in paper chromatography (see below). A satisfactory separation of a synthetic mixture of leucine, valine, alanine, glutamic acid, glycine, and aspartic acid (30 mg. of each) was obtained by using a cellulose column (31·7 × 3·0 cm.; cellulose content 115·5 g.), the only " overlaps " being between alanine and glutamic acid, and between glycine and aspartic acid.

(b) *Paper chromatography.* One-dimensional chromatography by the " descending " technique was used. Whatman No. 1 paper was employed, except where the separation of larger quantities of amino-acids was desired, for which Whatman No. 3 paper was used (see below). The chromatographic solvents chiefly used were: (*a*) aqueous phenol (containing 73·85% by wt. of phenol) in an atmosphere containing ammonia and hydrogen cyanide (Consden, Gordon, and Martin, *Biochem. J.*, 1944, **38**, 224); (*b*) the upper layer of butanol–acetic acid–water (4 : 1 : 5 vol.) (Partridge, *Biochem. J.*, 1948, **42**, 238); and (*c*) *tert.*-amyl alcohol in an atmosphere containing diethylamine (Work, *Biochim. Biophys. Acta*, 1949, **3**, 400). Each of these solvents was nearly but not quite saturated with water at 15—25°, so that a slight fall in temperature should not cause separation into two phases. The chromatograms were allowed to hang in the chromatographic tank for several hours before addition of the solvent to the glass trough

(Hanes and Isherwood, *Nature*, 1949, **164**, 1107). Pads of filter paper were clipped to the bottoms of chromatograms which were to be run for long periods (Hanes and Isherwood, *loc. cit.*). After development, chromatograms which were required for quantitative work (see later), or for which phenol had been used as solvent, were dried at room temperature (Fowden and Penney, *Nature*, 1950, **165**, 846; Novellie, *ibid.*, 1950, **166**, 1000; Brush, Boutwell, Barton, and Heidelberger, *Science*, 1951, **113**, 4); other chromatograms were usually dried at 50—80°. The spray reagent normally used to reveal the positions of the amino-acids was the acidified ninhydrin solution of Consden, Gordon, and Martin (*Nature*, 1948, **162**, 180). The Pauly reagent was used to confirm the presence of tyrosine and of histidine on the chromatograms, and Ehrlich's reagent for tryptophan. To detect cystine and cysteine, a portion of the solution was oxidised with hydrogen peroxide; the cysteic acid so formed is readily identified by its low R_F value in phenol (Dent, *Biochem. J.*, 1947, **41**, 240). Methionine is oxidised by hydrogen peroxide to its sulphone, which may be identified by chromatography with butanol–acetic acid (R_F 0·27).

For a more exhaustive examination than one-dimensional chromatograms can provide, we preferred the following technique to the use of two-dimensional chromatograms. A narrow band of the concentrated hydrolysate was developed (18 hr.) on Whatman No. 3 paper with butanol–acetic acid. Narrow strips, cut from the sides of the developed chromatogram, were sprayed with the ninhydrin reagent, and by reference to these " guide-strips " the chromatogram was cut transversely into strips. The amino-acids were eluted from each strip with distilled water by Dent's method (*loc. cit.*); subsequent treatment of the strips with ninhydrin showed that elution had been complete. Each eluate was separately concentrated and the amino-acids present were identified by one-dimensional chromatography. In this way the behaviour of the components in a variety of solvents and with varied reagents can be observed. The modifications required for quantitative work are described below.

Identification of the Amino-acids obtained by Acid Hydrolysis of Ascophyllum nodosum *and* Laminaria saccharina.—A portion of an acid hydrolysate of *A. nodosum* (prepared as previously described, and containing 0·046 g. of α-amino-acid nitrogen) was evaporated *in vacuo* below 50° and the residue was shaken with warm glacial acetic acid (4 × 25 ml.), the solution being separated each time by filtration. The combined filtrates were concentrated *in vacuo* and again filtered. The filtrate (9·6 ml.) was chromatographed on a cellulose column (27·7 × 3·7 cm.; cellulose content 128 g.) with the butanol–acetic acid mixture described above. The eluate was collected in fractions (3—4 ml.), each of which was examined for amino-acids by one-dimensional paper chromatography. Those identified were glycine, alanine, valine, leucine, *iso*leucine, phenylalanine, serine, threonine, aspartic acid, glutamic acid, proline, lysine, and arginine. The degree of separation of the amino-acids was poor, probably owing to the effect of contaminants in the extract.

An acid hydrolysate of *L. saccharina* (Sept., 1945) was treated as described above for *A. nodosum*, the only major difference being in a preliminary shaking of the *L. saccharina* hydrolysate with a small amount of activated charcoal (Partridge, *Biochem. J.*, 1949, **44**, 521) in an attempt to remove substances (*e.g.*, soluble humin) which might interfere with the chromatography. This treatment effected a slightly improved separation of the amino-acids. The amino-acids identified were the same as before. An attempt to detect tyrosine and phenylalanine in an extract of the charcoal (Partridge, *loc. cit.*) gave an indecisive result.

Electrodialysis of Hydrolysates.—The above hydrolysates of seaweed samples gave poor paper chromatograms. It was found that satisfactory chromatograms could be produced if the hydrolysates were subjected to preliminary treatment with charcoal (see above) followed by electrodialysis to remove electrolytes, and this procedure was followed in subsequent work. Electrodialysis was effected by Dent's modification (apparently unpublished) of the original apparatus of Consden, Gordon, and Martin (*Biochem. J.*, 1947, **41**, 590). The losses of amino-acids during the charcoal treatment and electrodialysis were evaluated by determination of the total α-amino-acid nitrogen of the hydrolysates before and after treatment; it was found possible to reduce the loss of α-amino-acid nitrogen in the combined procedures below 5% (see below).

Identification of the Amino-acids obtained by Acid Hydrolysis of Pelvetia canaliculata and Rhodymenia palmata.—An acid hydrolysate of the *P. canaliculata* (March, 1949) sample was prepared as already described. A portion of the crude hydrolysate (50 ml., containing 0·030 g. of α-amino-acid nitrogen) was gently shaken for 30 min. with activated charcoal (0·1 g.). The charcoal was removed by filtration and washed with water. The combined filtrates were concentrated *in vacuo* below 45°, and brought to pH 10—11 by aqueous sodium hydroxide. The solution was aerated vigorously for 2 hr. to remove ammonia (which interferes with electrodialysis), made just acid to litmus with hydrochloric acid, and then electrodialysed. The

current, initially 1 amp., decreased during 6·5 hr. to 0·085 amp., whereupon electrodialysis was discontinued. The solution was filtered from a very small residue, concentrated *in vacuo*, and made up to 50 ml. Ninhydrin–carbon dioxide determinations showed that the electrodialysed solution contained 95·1% of the α-amino-acid nitrogen originally present in the crude hydrolysate.

A portion of the electrodialysed hydrolysate was concentrated *in vacuo* at room temperature, and the amino-acids present were identified by the chromatographic procedures already described. In addition to those found in the acid hydrolysates of *A. nodosum* and *L. saccharina*, methionine, histidine, tyrosine, and ornithine were identified. Cystine was not found. Application of Crumper and Dent's technique (*Nature*, 1949, **164**, 441) showed that in each case the amino-groups were in the α-position.

An acid hydrolysate of *R. palmata* was treated as described above for *P. canaliculata*, the only major difference being that preliminary treatment of the crude hydrolysate with charcoal was unnecessary, the hydrolysate being much lighter in colour than that from *P. canaliculata*. The electrodialysed hydrolysate contained 96·1% of the total α-amino-acid nitrogen of the crude hydrolysate. The amino-acids identified were the same as those found in the *P. canaliculata* hydrolysate.

Alkaline Hydrolysis: Tests for Tryptophan and Di-iodotyrosine.—A portion (10 g.) of *P. canaliculata* (March, 1949) was heated under reflux with 5N-sodium hydroxide (200 ml.) for 6·5 hr. at 120—130°. The hydrolysate (a dark, opaque liquid) was brought to pH *ca.* 6 by the addition of hydrochloric acid, and the mixture was cooled. The gelatinous solid which separated on centrifugation was shaken with very dilute hydrochloric acid and again centrifuged. The combined extracts were made up to 500 ml. A portion (20 ml.) of this solution was freed from ammonium ions (see above) and electrodialysed; the filtered residual solution was evaporated *in vacuo* below 40° and the residue was taken up in a small volume of very dilute aqueous ammonia. A one-dimensional chromatogram of this solution was developed with butanol–acetic acid and sprayed with Ehrlich's reagent; a bright pink spot (R_F 0·55) revealed the presence of tryptophan. Di-iodotyrosine could not be detected on a similar chromatogram sprayed with the Pauly reagent, but this test was not regarded as conclusive, because a concentrated standard solution of di-iodotyrosine gave only faint spots under the same conditions.

An alkaline hydrolysate of *R. palmata* was similarly prepared and examined, with similar results.

Detection of D-*Amino-acids by Means of an Oxidase.*—We are grateful to Dr. H. Blaschko, of the Department of Pharmacology, for examining a solution which was obtained by acid hydrolysis of *P. canaliculata* (March, 1949); salts were removed by electrodialysis, and a few drops of toluene were added as a preservative. The oxidase was prepared from pig kidney (see, for example, Blaschko, *Biochem. J.*, 1949, **44**, 268). The hydrolysate (2·0 ml., containing 1·14 mg. of α-amino-acid nitrogen) was allowed to react in a Warburg apparatus at 37·5° with 0·6 ml. of the oxidase preparation, with the addition of 0·2M-sodium phosphate buffer (pH 7·4; 0·4 ml.). Two control experiments were run simultaneously; in these, the hydrolysate was replaced (*a*) by water (2·0 ml.) saturated with toluene, and (*b*) by 0·4M-DL-methionine (2·0 ml.) saturated with toluene. After 12 min., control (*b*) had absorbed 249 μl. of oxygen; after 150 min., the hydrolysate had absorbed 69 μl., and control (*a*) 31 μl., of oxygen. These results suggest that the hydrolysate contained small amounts of D-amino-acids, but the considerable variation in the rates of oxidation of D-amino-acids makes it impossible to draw quantitative conclusions. Under similar conditions, with 2·0 ml. of the following amino-acid solutions, the volumes of oxygen absorbed after 90 min. were: 0·008M-DL-aspartic acid, 86; 0·016M-DL-glutamic acid, 13; 0·004M-D-alanine, 79; 0·004M-D-valine, 117; 0·004M-D-leucine, 92; 0·004M-D-*iso*leucine, 97 μl.

Quantitative Determination of Amino-acids obtained by Hydrolysis of the Algae.—(a) *Procedure.* Before use in quantitative work, the Whatman No. 3 paper was thoroughly washed with a 0·1% (w/v) solution of 8-hydroxyquinoline in aqueous ethanol, then with 2N-acetic acid, and finally with distilled water. An apparatus of the type described by Hanes and Isherwood (*loc. cit.*) enabled a number of paper sheets to be treated simultaneously.

The quantitative separations were carried out on sheets *ca.* 50 cm. long and 23 cm. wide. An "Agla"-brand micro-syringe was used to apply an accurately known volume of the amino-acid solution to the central portion (13 cm.) of the "starting-line"; the width of the amino-acid band was kept small (*ca.* 0·5 cm.) by applying the solution in successive small portions (0·03—0·05 ml.), each portion being dried by gentle warming before application of the next. The total volume of solution applied was chosen to correspond to *ca.* 0·04—0·2 mg. of α-amino-acid nitrogen of each amino-acid to be determined. "Guide-spots" of the same solution were

applied 1—1·5 cm. from the extremities of the starting-line. After development, the chromatogram was allowed to dry, and washed if necessary (with an organic solvent) to remove traces of the developing solvent. A longitudinal strip of width 2—2·5 cm. was cut from each side of the chromatogram; these strips, on treatment with ninhydrin (or other suitable reagent) indicated the positions of the amino-acid bands on the main portion of the chromatogram. Transverse strips were cut from the latter to isolate the bands of the amino-acids which were to be determined, and these amino-acids were eluted from the strips by distilled water (Dent, *loc. cit.*). Subsequent treatment of the strips with ninhydrin indicated whether elution had been complete. The eluate from each strip was collected in the reaction-flask to be used for the subsequent determination (Van Slyke, MacFadyen, and Hamilton, *loc. cit.*); the solvent was removed *in vacuo* at room temperature, water (2 ml.) was added to the residue, the solution was brought to the appropriate pH, and the amino-acid was determined by the ninhydrin–carbon dioxide method. Strips cut from a blank chromatogram which had been developed and treated in the same way were also eluted; the extracts were submitted to the ninhydrin determination, and these blank experiments gave small corrections which were applied to each analysis.

(b) *Analysis of synthetic mixtures.* The accuracy was tested by experiments with known synthetic mixtures of (A) glutamic acid, glycine, and valine; and (B) glycine, valine, and phenylalanine, the chromatographic solvents used being respectively phenol (in the presence of ammonia) and butanol–acetic acid (see above). Development for 18 hr. was found to effect complete separation in both cases. The phenol chromatogram, when dry, was washed with dry ether; no washing was considered necessary in the other case. The blanks were found to be small and relatively constant. The results of the determinations are given in Table 4.

TABLE 4.

Synthetic mixture (A)	α-Amino-acid nitrogen			Synthetic mixture (B)	α-Amino-acid nitrogen		
	Found (mg.)	Calc. (mg.)	Found, as % of calc.		Found (mg.)	Calc. (mg.)	Found, as % of calc.
Glutamic acid ...	0·110	0·110	100	Glycine	0·093	0·095	98
Glycine	0·093	0·093	100	Valine	0·102	0·104	98
Valine	0·106	0·099	107	Phenylalanine	0·090	0·089	101

(c) *Analysis of hydrolysates of algae.* Certain amino-acids were determined in the electrodialysed solutions obtained by acid hydrolysis of *P. canaliculata* (March, 1949) and *R. palmata* (these solutions had been protected from micro-organisms by the addition of a few drops of toluene). Aspartic acid, glutamic, and alanine were separated by development (24 hr.) in phenol–ammonia; valine, leucine, and *iso*leucine by development (65 hr.) in *tert.*-amyl alcohol–diethylamine. The separation of valine and tyrosine was incomplete, and these two amino-acids were eluted and determined together. The results are given in Table 2, the values being the means of duplicate analyses.

1 : 3-*Dibromo*-2-*chloro*-5-*nitrobenzene*.—Bromination of *p*-nitroaniline (Shepherd, *J. Org. Chem.*, 1947, **12**, 275) gave 2 : 6-dibromo-4-nitroaniline (m. p. 200—202°; 96%), which was diazotised (Hodgson and Walker, *J.*, 1933, 1620) and converted into the chloro-compound (m. p. 89·5—91°; 70%) by the Sandmeyer method. The last compound failed to react with potassium fluoride under the conditions of Cook and Saunders (*Biochem. J.*, 1947, **41**, 558).

1-*Bromo*-2-*fluoro*-3 : 5-*dinitrobenzene*.—Bromination of 2 : 4-dinitroaniline (I. G. Farbenind. A.-G., B.P. 399,769/1933) gave 2-bromo-4 : 6-dinitroaniline (m. p. 145—148°; 57%) which was diazotised (Hodgson and Walker, *loc. cit.*) and converted into 1-bromo-2-chloro-3 : 5-dinitrobenzene (m. p. 58—59°; 66%) by the Sandmeyer method. The chloro-compound reacted with potassium fluoride under the conditions of Cook and Saunders (*loc. cit.*) to give 1-*bromo*-2-*fluoro*-3 : 5-*dinitrobenzene*. Recrystallisation from ether and then from aqueous ethanol gave pale yellow needles, m. p. 69° (46%) (Found: C, 27·6; H, 0·8; N, 10·6; Br, 30·2. $C_6H_2O_4N_2BrF$ requires C, 27·2; H, 0·8; N, 10·6; Br, 30·2%).

2-*Bromo*-4 : 6-*dinitrophenyl Derivatives of Glycine and of Glycyl-peptides*.—The amino-acid or peptide was shaken at room temperature with an excess of 1-bromo-2-fluoro-3 : 5-dinitrobenzene in aqueous-ethanolic solution containing sodium hydrogen carbonate. After removal of ethanol *in vacuo* below 35°, the solution was shaken with ether to remove excess of reagent. Acidification of the aqueous layer yielded the desired derivative as a yellow or orange solid, which was recrystallised from methanol or aqueous methanol below 50°. Thus were prepared 2-*bromo*-4 : 6-*dinitrophenyl-glycine*, m. p. 181·5° with previous sintering (Found: C, 30·2;

H, 2·2; Br, 25·1. $C_8H_6O_6N_3Br$ requires C, 30·0; H, 1·9; Br, 25·0%), and *-glycylglycine*, m. p. 191° with previous sintering (Found: C, 31·7; H, 2·7; N, 14·5; Br, 20·8. $C_{10}H_9O_7N_4Br$ requires C, 31·85; H, 2·4; N, 14·9; Br, 21·2%). Crystalline solids corresponding to the 2-bromo-4 : 6-dinitrophenyl derivatives of triglycine, tetraglycine, and leucylglycine (m. p.s respectively 187°, 214°, and 80°, all with previous sintering) were prepared in small quantity, but purification was difficult and analytically pure samples were not obtained.

Paper chromatography of the above compounds, with butanol–acetic acid, phenol (with and without ammonia), and butanol as solvents, gave unsatisfactory results.

2-Bromo-4 : 6-dinitrophenyl-peptides from Pelvetia canaliculata.—(*Note:* In this section, the prefix " 2-bromo-4 : 6-dinitrophenyl-" has been abbreviated to " BDNP-"). The seaweed sample (March, 1949; 280 g.) was mechanically shaken for 25 hr. at room temperature with 0·05N-sodium hydroxide (1·5 l.). The residue obtained on centrifugation and filtration through cloth was shaken for a further 4 hr. with fresh solvent (0·5 l.), and the mixture was again centrifuged and filtered through cloth. The combined filtrates (*ca.* 1 l.) were shaken with ethanol (250 ml.) and centrifuged, and the liquid was filtered., The filtrate was saturated with solid carbon dioxide and sodium hydrogen carbonate (10 g.) was added. Determinations on aliquot portions of the solution indicated that it contained 13% of the total nitrogen of the original seaweed. A solution of 1-bromo-2-fluoro-3 : 5-dinitrobenzene (5 g.) in ethanol (50 ml.) was added, and the mixture was kept at 40—50° for 23 hr., with mechanical stirring for the first 11 hr. Evaporation *in vacuo* at 40—50° gave a solution (*ca.* 250 ml.) which was centrifuged, a small residue being rejected. The yellow turbid supernatant liquid was diluted with water (250 ml.) and shaken with ether (3 × 500 ml.) to remove excess of bromofluorodinitrobenzene. The aqueous layer (which separated with difficulty, owing to the tendency to form an emulsion) was concentrated *in vacuo* at 40—50°, and after centrifuging a very small residue was rejected. The turbid liquid was acidified with hydrochloric acid, and centrifuged again, a gelatinous solid separating in small amount (this was later investigated by the methods described below, and was found to contain only very small amounts of BDNP-peptides). Almost one-half of the supernatant liquid was used in attempts to isolate BDNP-peptides, and eventually the following method was adopted. The remainder of the liquid (which was acid to litmus but not to Congo-red) was shaken with a solution of mercuric acetate (50 g.) in water (250 ml.); centrifugation of the resulting mixture yielded a solid, probably consisting largely of mercuric salts of BDNP-peptides. (On neutralisation with sodium carbonate the supernatant liquid yielded further solid, but this was later found to contain only very small amounts of BDNP-peptides.) The solid was washed twice with water by decantation; its aqueous suspension was then saturated with hydrogen sulphide, and the mercuric sulphide was removed by filtration; excess of hydrogen sulphide was removed from the filtrate by evaporation *in vacuo* below 35°. The mixture of BDNP-peptides contained in the resulting solution was fractionated by successive extraction with ethyl acetate and butanol, followed by counter-current partition between 5% aqueous ammonia and butanol (cf. Woolley, *J. Biol. Chem.*, 1949, **179**, 593). The partition was carried out in a series of centrifuge-tubes, as centrifugation was necessary at each stage to separate the liquid layers. 15 Ml. of each solvent were used in each tube, and the lower layers were transferred each time by means of a suitable pipette. The colour peaks were judged visually against a white background. The ethyl acetate extract (A), after partition in a system of 20 tubes, gave colour peaks in tubes 1—3 (upper layers), 11—14 (both layers) and 18—20 (lower layers), and from these fractions were obtained, respectively, the sticky yellow-brown solids A1 (13·5 mg.), A2 (22 mg.), and A3 (35·5 mg.). The butanol extract (B) was partitioned in a system of 10 tubes; colour peaks were observed in tubes 1—3 (upper layers) and 9—10 (lower layers) which yielded, respectively, the sticky brown solids B1 (11 mg.) and B2 (89 mg., probably containing a high proportion of inorganic salt). The fractions A1, A2, A3, B1, B2, and also the fraction C (obtained on evaporation of the faintly yellow aqueous solution left after extraction with ethyl acetate and butanol), were hydrolysed by boiling them under reflux with 6N-hydrochloric acid for 12 hr. The hydrolysates were shaken with ether. All *N*-terminal amino-acids present in the original BDNP-peptides should now have been present in the ethereal layers as the BDNP derivatives; the remaining amino-acids, including the mono-BDNP derivatives of diamino-acids, should have been retained in the aqueous layer. Each ethereal layer was evaporated, and the residues (if any) were hydrolysed by aqueous ammonia (*d* 0·88) at 100—110° for 4 hr.; this procedure (Lowther, *Nature*, 1951, **167**, 767) has been reported to liberate the free amino-acids (except cystine and arginine) from their DNP derivatives, and it seemed likely that the BDNP derivatives would behave in the same way. The hydrolysates were examined for amino-acids by paper chromatography; the results were negative except in the solutions

from fractions A2 and A3, for which serine and glycine, and glycine, respectively, were identified as *N*-terminal amino-acids.

The amino-acids in the aqueous layers of the acid hydrolysates of the BDNP-peptide fractions were identified by paper chromatography; the hydrolysates were then evaporated and the residues hydrolysed with concentrated aqueous ammonia as described above, to hydrolyse any mono-BDNP derivative of a diamino-acid. The products were then examined chromatographically for basic amino-acids. The results are given in Table 3.

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504. *Hydrazine. Part IV.* The Bromostannates and Bromostannites of Hydrazine, Dimethyl Ketazine, and Pentan-3-one Hydrazone.*

By W. PUGH.

(*With Notes on the Optical Properties of the Crystals.* By H. C. G. VINCENT.)

Dihydrazinium hexabromostannate, hydrazinium tribromostannite, and dihydrazinium tetrabromostannite have been prepared. These salts, or mixtures of tin bromides and hydrazine hydrobromide, yield on treatment with acetone and diethyl ketone the bromostannates and bromostannites of dimethyl ketazine and pentan-3-one hydrazone respectively.

DIHYDRAZINIUM CHLOROSTANNATE has been described recently (Part I, *J.*, 1952, 4138) and shown to form compounds with aliphatic ketones. These compounds were at first reported as ketone addition compounds, but were subsequently (Part II, *J.*, 1953, 354) shown to be chlorostannates of dimethyl ketazine and of certain hydrazones acting as bases. No salts of such bases had hitherto been described.

Similar bromostannates and bromostannites have now been prepared from mixtures of the tin bromides and hydrazine hydrobromide, in aqueous solution (hydrazine salts), and in acetone–water and diethyl ketone–water mixtures respectively (ketazinium and hydrazonium salts). Mixtures of the simple salts also dissolved in ethyl methyl and di-*n*-propyl ketones, forming viscous solutions, but these could not be induced to crystallise, even after several months at −10°. It was noted that the chlorostannates (Part II, *loc. cit.*) also separated with increasing difficulty from these same ketones.

Like the corresponding chlorostannates, these ketazinium and hydrazonium salts hydrolyse completely in acid solution, forming hydrazinium ions and free ketone. It was thus possible to estimate the hydrazine formed by Andrews's method. The figures quoted for nitrogen in the Experimental section were obtained in this way. In one case, also, the acetone was distilled and estimated by Messinger's method (Goodwin, *J. Amer. Chem. Soc.*, 1920, **42**, 39; Cassar, *Ind. Eng. Chem.*, 1927, **19**, 1061).

EXPERIMENTAL

Dihydrazinium Hexabromostannate.—Tin foil (3 g.) was added in small pieces to an excess of well-cooled bromine and, after the addition of hydrobromic acid (48%; 6 c.c.) and water (4 c.c.), the excess of bromine was removed by boiling. Hydrazine hydrate (28%; 8 c.c.) was then added and the clear yellow solution was crystallised over sodium hydroxide. Successive crops, dried on filter-papers and *in vacuo*, had identical composition and were free from contamination with hydrazine hydrobromide (compare the preparation of the chlorostannate, Part II, *loc. cit.*) [Found: N_2H_4, 9·6; Br, 72·0; Sn, 17·9. $(N_2H_5)_2SnBr_6$ requires N_2H_4, 9·6; Br, 72·2; Sn, 17·9%]. The same *salt* was obtained, after long storage, from the mother-liquors of the crystallisation of the ketazinium bromostannate described below.

The crystals are orthorhombic, being yellow rectangular plates (colourless in microscope

* Part III, *J.*, 1953, 1934.

mounts) without pronounced cleavage. The optic axial plane is parallel to the surface of the plates, with $Bx^{\alpha}(\gamma)$ parallel to the elongation, the plates giving an optic normal figure. They are optically positive, with small $2V$ of about 20°. Dispersion is fairly strong, red > violet. Elongation is positive. Refractive index of (*a*) is considerably above 1·84 and beyond the range of suitable immersion liquids. Double refraction is also extreme.

The salt deliquesces in damp weather only, and it decomposes on heating, with partial sublimation. It is insoluble in ether, benzene, chloroform, carbon tetrachloride, and light petroleum, but very soluble in water. Concentrated aqueous solutions remain clear when kept, but dilution causes precipitation of gelatinous tin hydroxide. The salt reacts with and dissolves in the simple aliphatic ketones, forming ketazinum and hydrazonium bromostannates.

Bis(dimethyl Ketazinium) Hexabromostannate.—A solution of stannic bromide and hydrazine monohydrobromide in aqueous hydrobromic acid, prepared from tin (3 g.) as described above, was treated with twice its volume of acetone. Much heat was liberated and the clear yellow solution slowly deposited yellow rhombs which, after being recrystallised from acetone–water (4 : 1) and dried *in vacuo*, had m. p. 138—139° [Found: C, 17·4; H, 3·2; N, 6·8; Br, 58·0; Sn, 14·5. $(C_6H_{13}N_2)_2SnBr_6$ requires C, 17·5; H, 3·2; N, 6·8; Br, 58·2; Sn, 14·5%]. The same *salt* was obtained by adding acetone to the mother-liquors from the crystallisation of dihydrazinium hexabromostannate.

The crystals are orthorhombic or monoclinic, with ill-defined platy habit. There is no cleavage or twinning apparent and the optic axial plane is probably parallel with the plates. Optically positive. $2V^{\gamma} = 60°$. Dispersion is weak or absent. Refractive indices (D): $\alpha = 1{\cdot}623$, $\beta = 1{\cdot}654$, $\gamma = 1{\cdot}758$. Double refraction is extreme, $\gamma - \alpha = 0{\cdot}135$.

The salt resembles the preceding one in solubility and deliquescence. Its aqueous solution readily decomposes, losing acetone and slowly depositing dihydrazinium hexabromostannate. Acetone may be completely distilled out, and estimated in the distillate, 4 moles being recovered per mole of salt.

Bis(pentan-3-one Hydrazonium) Hexabromostannate.—The mother-liquors from the crystallisation of dihydrazinium hexabromostannate were treated with diethyl ketone until, after shaking, the mixture separated into two layers. Much heat was generated and when the mixture was cooled the lower layer yielded large yellow needles of the *hexabromostannate*, m. p. 162—163° (decomp.) [Found: C, 15·0; H, 3·3; N, 7·0; Br, 59·8; Sn, 14·8. $(C_5H_{13}N_2)_2SnBr_6$ requires C, 15·0; H, 3·3; N, 7·0; Br, 59·9; Sn, 14·9%].

The crystals are monoclinic, being deep yellow, needle-like prisms (colourless by transmitted light in microscopic mounts) greatly elongated parallel to *c*, with perfect longitudinal fibrous cleavage. Twinning is absent. The optic axial plane is perpendicular to (010) and to the elongation direction. $\widehat{\beta c} = 14°$. Optically negative. $2V^{\alpha}(D) = 73°$. Dispersion is slight, red > violet. Elongation negative or positive. Refractive indices (D): $\alpha = 1{\cdot}652$, $\beta = 1{\cdot}701$, $\gamma = 1{\cdot}729$. Birefringence high, $\gamma - \alpha = 0{\cdot}077$.

The salt is insoluble in common organic solvents and it is much more susceptible than the dimethyl ketazinium salt to the hydrolytic action of moisture. It smells strongly of diethyl ketone in moist air.

Hydrazinium Tribromostannite.—Anhydrous stannous bromide (2·8 g., 1 mol.) and hydrazine monohydrobromide (1·14 g., 1 mol.) were dissolved in warm water (2 c.c.), yielding a pale yellow solution which gave a thick magma of crystals at 0°. Nearly all the solid redissolved, however, on attempted filtration. Better control of crystallisation was secured by dissolving the same quantities in 50% aqueous alcohol (5 c.c.); subsequent cooling then yielded pearly, white, micaceous plates which were filtered off and washed under suction, successively with 70% alcohol and absolute alcohol, and dried *in vacuo* (Found: N_2H_4, 8·3; Br, 61·1; Sn, 30·2. $N_2H_5SnBr_3$ requires N_2H_4, 8·2; Br, 61·3; Sn, 30·4%). The *salt* is very deliquescent when moist and oxidises rapidly in air, becoming yellow. Once properly dried, however, it is not unduly deliquescent, nor does it oxidise so readily. It swells considerably at about 150° and decomposes with vigorous gas evolution at 180°.

The crystals are orthorhombic plates and scales with pronounced basal cleavage. The optic axial plane and $Bx^{\alpha}(\gamma)$ are normal to the plane of the plates. Optically positive. $2V = 35$—40° approx. Axial dispersion is strong, red < violet, giving anomalous blue interference tints for sections normal to Bx^{α}. The refractive index of α is considerably above 1·84 and is beyond the range of suitable immersion media. The birefringence is moderate.

Dihydrazinium Tetrabromostannite.—Anhydrous stannous bromide (2·8 g., 1 mol.) and hydrazine monohydrobromide (3·4 g., 3 mols.) were dissolved in warm water (3 c.c.), and the solution was mixed with alcohol (10 c.c.). On being cooled the lower layer crystallised, forming

yellowish rectangular prisms which were washed with alcohol and dried *in vacuo* [Found: N_2H_4, 12·4; Br, 61·1; Sn, 22·8. $(N_2H_5)_2SnBr_4,H_2O$ requires N_2H_4, 12·2; Br, 61·3; Sn, 22·8%]. Crystallisation of mixtures containing smaller proportions of hydrazine bromide from more dilute alcoholic solutions yielded products which were obviously mixtures of the tribromo- and the tetrabromo-stannite, the final fractions, obtained from liquors containing the alcohol washings, tending towards pure tetrabromostannite.

The *salt* is deliquescent and is oxidised readily in moist air. It softens at 60° and melts at 81—83°. It suffers no loss in weight during several days over sulphuric acid *in vacuo*. It is decomposed by water, yielding gelatinous tin hydroxide; it is soluble in dilute acids, and in acetone, but insoluble in other common organic solvents. The crystals are orthorhombic, being usually stout prisms modified by pinacoid faces, but bladed and greatly elongated platy forms occur. They have no pronounced cleavage. The optic axial plane is parallel to the elongation and the α bisectrix is normal to the surface of the plates; elongation is positive. $2V(\alpha) = 85°$ (approx.). Optically negative; axial dispersion is weak, with red < violet in the bisectrix containing α. The refractive indices are beyond the range of immersion media; birefringence is rather high.

Dimethyl Ketazinium Tribromostannite.—Molar proportions of stannous bromide (1·4 g.; freshly prepared and anhydrous) and hydrazine monohydrobromide (0·6 g.) were dissolved in a mixture (2 c.c.) of equal volumes of ethanol and acetone, and the solution was then shaken with an equal volume of ether. The mixture, on being kept at 0° for several hours, yielded colourless plates which, after being washed with cold alcohol–ether and finally with ether, and dried, *in vacuo*, had m. p. 52—54° (Found: N, 5·7; Br, 49·0; Sn, 24·1; C_3H_6O, 24·6. $C_6H_{13}N_2SnBr_3,H_2O$ requires N, 5·7; Br, 49·0; Sn, 24·3; C_3H_6O, 23·7%). The crystals lose water (4% by weight) on desiccation over sulphuric acid. The same *salt*, m. p. 53—54°, was obtained during an attempt to make bis(dimethyl ketazinium) tetrabromostannite from molar proportions (1 : 2) of the simple salts, and crystallising from warm acetone–water (4 : 1). [Bis-(dimethyl ketazinium) tetrabromostannite was not obtained in any circumstances in this work.]

The salt occurs as monoclinic or triclinic, ill-shaped plates, with poor cleavage parallel to the plates. One optic axis emerges nearly perpendicular to the plates. $2V(D) = 90°$ (approx.). The axial dispersion is moderate, red > violet in the γ bisectrix, and horizontal dispersion is distinct. Refractive indices (D): $\alpha = 1·65$, $\beta = 1·72$, $\gamma = 1·79$. These values are approximate only, because the crystals are attacked slightly by immersion liquids.

The authors thank Mr. R. von Holdt, B.Sc., for carrying out the carbon and hydrogen estimations.

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505. *Hydrazine. Part V.* Complex Halides of Aluminium and Hydrazine.*

By W. Pugh and M. C. B. Hotz.

(*With Notes on the Optical Properties of the Crystals.* By H. C. G. Vincent.)

Hydrazinium hexachloro- and hexabromo-aluminates are described. These compounds are unique, being the only known compounds in which aluminium is 6-covalent with chlorine and bromine. Attempts to make similar compounds of some ketazines and hydrazones were not successful. The reported existence of anhydrous hydrazinium hydrogen pentafluoroaluminate is confirmed, no other complex fluoride having been obtained. Corresponding iodoaluminates could not be isolated.

Hückel ("Structural Chemistry of Inorganic Compounds," translated by Long, Elsevier Publ. Co., Amsterdam, 1950, Vol. I, p. 168, footnote) states, without giving references, that compounds of the type $M^I_3AlCl_6$ exist and contain $[AlCl_6]^{3-}$ ions; Sidgwick ("The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, Vol. I, p. 435) maintains that only fluorine gives aluminium a covalency of more than 4. The original

* Part IV, preceding paper.

literature contains, to our knowledge, only one reference to the preparation of compounds of the above type, Baud (*Ann. Chim. Phys.*, **1904**, **1**, 8) claiming to have isolated both sodium and potassium hexachloroaluminate. However, the existence of these compounds was not confirmed by the later work of Kendall, Crittenden, and Miller (*J. Amer. Chem. Soc.*, 1923, **45**, 963) who, by an extensive thermal analysis of 41 systems, established the identity of 53 compounds, all of the general type $xAlX_3,yM^{n+}X_n$ (X = Cl or Br); in the individual formulations, y never exceeds x, and in the majority, $y = x$ or $0{\cdot}5x$ (*i.e.*, $M^I[AlX_4]$, $M^{II}[AlX_4]_2$). It is probable, then, that aluminium is 4-covalent in all of them, and it has not hitherto been clearly established that aluminium can be 6-covalent in such compounds. It is well known to be 6-covalent in complex fluorides, and also in aluminium chloride (Ketelaar, Macgillavry, and Renes, *Rec. Trav. chim.*, 1947, **66**, 501).

The preparation of hexachloro- and hexabromo-aluminates of hydrazine, described below, shows clearly for the first time that aluminium can be 6-covalent towards chlorine and bromine in complex salts. The compounds are typically salt-like and probably contain discrete $[AlCl_6]^{3-}$ and $[AlBr_6]^{3-}$ ions in the crystal lattice. Another new feature is that they were isolated as hydrates from aqueous solution. All the chloro- and bromo-aluminates previously described were obtained either by fusion methods (Baud, *loc. cit.*; Kendall *et al.*, *loc. cit.*; Friedman and Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 2236), or from non-aqueous solutions (Friedman *et al.*, *loc. cit.*; Jakubson, *Ber. Inst. Chem. Acad. Wiss., Ukraine*, 1940, **7**, 13, 17; Plotnikov and Gorenbein, *J. Gen. Chem., U.S.S.R.*, 1935, **5**, 1108), and statements that such compounds cannot be isolated from aqueous media are found in authoritative texts (Sidgwick, *op. cit.*; Moeller, "Inorganic Chemistry," J. Wiley and Sons, Inc., New York, 1952, p. 766).

It is possible that previous failure to prepare such compounds is due, not to the inability of the aluminium atom to co-ordinate six chlorine, or even bromine, ions, but, in part at least, to solubility relations. The simple hydrazine halides are very soluble in water, like the aluminium halides. Our own attempts to crystallise ammonium hexabromo-aluminate, by the method used for the hydrazine salt, failed, because the less soluble ammonium bromide fractionated out. It may well be that similar attempts using other very soluble halides (lithium, magnesium, calcium, zinc) would be successful.

A pentafluoroaluminate of hydrazine, but of somewhat variable composition, has been described by Weinland, Lang, and Fikentscher (*Z. anorg. Chem.*, 1926, **150**, 47) as a non-crystalline powder. A few other pentafluoroaluminates are known, but some of them are hydrated and probably contain $[AlF_5 \leftarrow\!\!- H_2O]^{2-}$ ions. It seemed desirable, therefore, to characterise the hydrazine salt more fully, and to determine whether it exists in a hydrated form. The only complex fluoride that could be obtained, however, was the anhydrous salt, described by the above authors, but it was obtained as a pure, crystalline product whose optical properties have been studied.

While mixtures of the tin halides with hydrazine halides have been shown (*J.*, 1953, 354, 1934) to react with ketones to form crystalline halogeno-stannates and -stannites of dimethyl ketazine and of some hydrazones, similar compounds were not obtained with aluminium chloride. One possible reason is the well-known catalytic activity of aluminium chloride in promoting the condensation of hydrazine and acetone to 3 : 5 : 5-trimethyl-pyrazoline. It was also not possible to isolate iodoaluminates of hydrazine, which is not surprising when only two iodoaluminates, $NaAlI_4$ and $KAlI_4$, are reported in the literature (Weber, *Pogg. Ann.*, 1857, **101**, 465; **103**, 259).

Experimental

Trihydrazinium Hexachloroaluminate Hexahydrate.—Approximately molar proportions of aluminium chloride and hydrazine monohydrochloride were dissolved in the minimum amount of water, and the concentrated solution was evaporated slowly over sulphuric acid and solid sodium hydroxide, yielding colourless rhombs or prisms which, dried on paper and *in vacuo*, had d_{17}^{17} 1·55 [Found: N_2H_4, 21·2; Cl, 47·4; Al, 6·0. $(N_2H_5)_3AlCl_6,6H_2O$ requires N_2H_4, 21·4; Cl, 47·5; Al, 6·0%]. When larger proportions of hydrazine hydrochloride were used (*e.g.*, 3 : 1 mol. ratio, theoretically required), hydrazine dihydrochloride separated first and it was necessary to resort to fractional crystallisation.

Trihydrazinium hexachloroaluminate hexahydrate undergoes partial melting, probably partial solution in its own water of hydration, at 142°, the melt clearing at 194—196°. At 20° the salt is stable, undergoing no loss in weight when kept over sulphuric acid for several days, but at 100° in air it loses both water and hydrogen chloride, leaving a mixture of hydrazine hydrochloride and hydrated aluminium oxide. It is very soluble in water and deliquescent, but it is insoluble in ether, alcohol, benzene, chloroform, carbon tetrachloride, and light petroleum.

The crystals are trigonal, stout prisms, often highly modified, or appear to be perfect rhombohedra, sometimes with small prism faces. There is no cleavage. Prismatic crystals are length positive. Optically positive. Refractive indices (D): $\omega = 1{\cdot}564$; $\varepsilon = 1{\cdot}588$.

Trihydrazinium Hexabromoaluminate Hexahydrate.—Quantities of hydrazine monohydrobromide and aluminium bromide (mol. ratio, 3 : 1), when crystallised together from aqueous solution, yielded clear, transparent prisms of pure *trihydrazinium hexabromoaluminate hexahydrate*, d_{17}^{17} 2·25 [Found: N_2H_4, 13·3; Br, 67·3; Al, 3·8. $(N_2H_5)_3AlBr_6,6H_2O$ requires N_2H_4, 13·4; Br, 67·3; Al, 3·8%]. When less than 3 mols. of hydrazine bromide were used per mol. of aluminium bromide, the same product was obtained, but it was always contaminated with aluminium bromide.

Like the chloroaluminate, it decomposes and dissolves partly in its water of crystallisation at 150°, forming a clear melt at 192°. It is quite stable at 20°, undergoing no loss in weight in the course of several days over sulphuric acid. It is very soluble in water, and deliquescent; it loses both water and hydrogen bromide when heated in air. The crystals are stout modified prisms, blades, or often rhomb-shaped plates. Cleavage is absent. $2V(\gamma) = 0°$ or near 0°. Optically positive. The plates give symmetrical extinction, an off-centred figure, and the shorter diagonal yields the γ index. Extinction on the blades is often oblique. The crystals may be trigonal but are probably monoclinic. Because of their extreme sensitiveness to moisture, optical measurements were difficult to make. Refractive index (D): $\omega = 1{\cdot}634$ (approx.). Birefringence low.

The complex ions in both these salts are considerably broken down in aqueous solution, the molecular conductivity at finite dilution reaching values which are characteristic of salts of the type AB_3 at infinite dilution. The molecular conductivities, μ, at 25° of the chloroaluminate (*A*) and bromoaluminate (*B*) at different dilutions (v l.) are:

v	5	25	50	125	500	625	3125
μ (*A*)	375	517	—	615	—	695	765
μ (*B*)	480	—	610	—	735	—	—

Hydrazinium Hydrogen Pentafluoroaluminate.—Solutions of aluminium fluoride, made from freshly precipitated aluminium hydroxide, and hydrazine dihydrofluoride were mixed, and the precipitate was filtered off, washed, and dried for several hours *in vacuo* over sulphuric acid. The fluorine was estimated by Willard's method (*Ind. Eng. Chem. Anal.*, 1936, **5**, 7) (Found: N_2H_4, 20·4; F, 60·6; Al, 17·4. Calc. for $N_2H_5,HAlF_5$: N_2H_4, 20·5; F, 60·9; Al, 17·4%). Varying the proportions of hydrazine fluoride and aluminium fluoride, temperature of precipitation, concentration of the reagents, and the period of digestion, had no effect on the composition. Variable results were obtained, however, when metallic aluminium (reagent grade, which was not completely soluble in hydrofluoric acid) was used as source of aluminium fluoride.

The salt is only sparingly soluble in water. The crystals are monoclinic, being colourless, much elongated plates and needles, too minute to yield exact optical data. The extinction angle is 25°, and the crystals are length slow. Refractive index for β is approximately 1·43; birefringence is fairly low.

We are indebted to Mr. I. R. Morrison for carrying out the conductance measurements.

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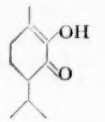
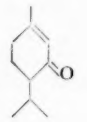
506. *The Dipole Moment and Infra-red Spectrum of Diosphenol.*

By R. J. W. Le Fèvre, F. Maramba, and R. L. Werner.

The dipole moments and infra-red spectra of diosphenol, piperitone, etc., are examined in relation to the same properties of tropolones.

This note records an examination of diosphenol (I), made as a result of other investigations on enols (cf. Hukins and Le Fèvre, *J.*, 1949, 898; Le Fèvre and Welsh, *J.*, 1949, 1909, 2230; Angyal and Le Fèvre, *J.*, 1950, 562).

(I)   (II)

Experimental

Piperitone (II), having been purified for other work (Le Fèvre and Maramba, *J.*, 1952, 235), was oxidised by 2% potassium permanganate solution as detailed by Penfold (*J. Proc. Roy. Soc. N.S.W.*, 1921, **55**, 139) and the steam-distilled product, after drying, sublimed, giving diosphenol (I) as needles, m. p. 82°, in *ca.* 5% yield. Camphorquinone, required below for comparative purposes, was prepared by selenium dioxide oxidation of the parent ketone (Evans, Ridgion, and Simonsen, *J.*, 1934, 137°).

The infra-red absorption spectra were determined on a Hilger D.209 spectrometer operated as a single-beam instrument with rock-salt prisms and photographic recording or on a Perkin-Elmer instrument, Model 12C, with similar optics and a " Brown " recorder. The frequency calibration was made through the ammonia and atmospheric absorption features catalogued by Oetjen, Kao, and Randall (*Rev. Sci. Instr.*, 1942, **13**, 515) for a sodium chloride prism; the degree of resolution between 5 and 13 μ by both instruments compared satisfactorily with that shown in spectra reproduced in the paper just cited.

Table 1. *Densities and dielectric constants of benzene solutions at 25°.*

10^6w_2	ε^{25}	d_4^{25}	$\alpha\varepsilon_1$	βd_1	10^6w_2	ε^{25}	d_4^{25}	$\alpha\varepsilon_1$	βd_1
0	2·2725	0·87378	—	—			*Camphorquinone.*		
		Diosphenol.			2,321	2·3027	0·87421	13·0	0·185
4,709	2·3014	0·87419	6·14	0·087	2,604	2·3068	0·87425	13·2	0·180
7,909	2·3175	0·87459	5·68	0·101	8,220	2·3820	0·87518	13·3	0·170
8,567	2·3256	0·87452	6·08	0·098	15,485	2·4704	0·87619	12·8	0·156
12,890	2·3474	0·87509	5·81	0·102					
13,744	2·3531	0·87509	5·86	0·091					
22,969	2·4093	0·87610	5·96	0·101					

Whence $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 5·92$, and $\Sigma(d_{12} - d_1)/\Sigma w_2 = 0·097_5$

Whence $\Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2 = 12·99$, and $\Sigma(d_{12} - d_1)/\Sigma w_2 = 0·164_5$.

Table 2. *Calculation of apparent dipole moments.*

Solute	M_2	$\alpha\varepsilon_1$	β	$_\infty P_2$ (c.c.)	$(R_L)_D$ (c.c.)	μ(D)
Diosphenol	168·2	5·92	0·112	238·2	48·8 *	$3·0_4$
Camphorquinone	166·2	12·99	0·188	452·1	44·3 †	$4·4_6$

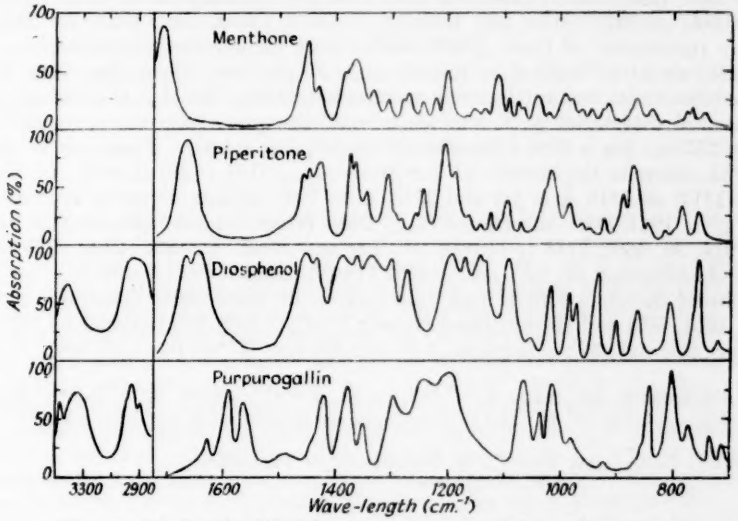
* Observed by von Auwers (*Ber.*, 1924, **57**, 1106).
† Calc. from constants listed by Vogel (*J.*, 1948, 1842).

Table 1 lists the measurements, on solutions in benzene at 25°, which lead to the dipole moments reported in Table 2. Symbols, methods, apparatus, etc., are as described in *Trans. Faraday Soc.*, 1950, **46**, 1, and *J.*, 1948, 1949, except that subscripts 1 and 2 now refer to solvent and solute respectively. This is the reverse of the convention previously followed in these laboratories (cf. *J.*, 1952, 1932).

Discussion.—Guenther (" The Essential Oils," van Nostrand, New York, 1950, Vol. II, p. 542) has summarised past suggestions regarding the correct formulation of diosphenol. The keto–enol structure (I) seems most favoured, although diketo- and dienol variants

have been proposed. The last type has been particularly supported more recently by Straneo (*Gazzetta*, 1940, **70**, 27; 1941, **71**, 646).

However, the polarity now found for diosphenol (*viz.*, 3·0—3·1 D) is higher than that to be expected, by analogy, for the dienol: we note that the moment of ethylene glycol is around 2·3 D, while those of the *cis*- and *trans-cyclo*hexane-1 : 2-diol are 2·3 and 2·4 D respectively (Svirbely and Lander, *J. Amer. Chem. Soc.*, 1950, **72**, 3756). Our original intention was to take the moment of camphorquinone (4·5 D) as an estimate of that of the diketo-isomer of (I), but this may not be safe because while the skeleton of a diketo*cyclo*hexane derivative is probably flexible (cf. Le Fèvre and Le Fèvre, *J.*, 1935, 1696; 1938, 494), that of a camphane derivative must be locked. It is relevant that Svirbely and Lander (*loc. cit.*) find both *cyclo*hexane-1 : 2-dione (2·8 D) and 2-hydroxy*cyclo*hexan-1-one (2·9 D) to have moments of the order of that (3·0 D) now given for diosphenol.



The wave-length scale at the left refers to the insets on the two lower curves.

The infra-red spectra are more informative: diosphenol cannot be wholly dienolic as a solid since not only does it absorb intensely at 1668 cm.$^{-1}$, very close to the ketonic frequency at 1666 cm.$^{-1}$ observed with piperitone, but also strongly at 3410 cm.$^{-1}$, *i.e.*, in the region where hydroxyl groups should display themselves. Dissolution of (I) or (II) in benzene or dioxan revealed no notable change with (II): the situation with (I) may be summarised:

Diosphenol	HO bands	C=O bands	C=C bands
Nujol mull	3410 (strong, fairly sharp)	1668	1645 (both strong)
Soln. in dioxan *	3410 (medium, broad)	1669	1646 (1646 stronger)
Soln. in benzene *	3460 (medium, sharp)	1675	1646 (relative strengths as in dioxan, but more so)

* Spectrum not reproduced.

These details have some resemblance to those found by Flett (*J.*, 1948, 1441) for, *e.g.*, 1 : 3-dihydroxyanthraquinone. In general, however, the infra-red spectroscopic evidence supports the representation of diosphenol as (I).

When this work was begun we though that (I) might serve as a guide to the, then unknown, polar and spectral properties of tropolone, since both contain the unit C=C(OH)·CO·C, although in the latter this is further conjugated. Allowing for the last fact by expecting $\mu_{C=O}$ in tropolone to be increased over that in diosphenol as that in piperitone is over that in *cyclo*hexanone (*viz.*, by *ca.* 0·7 D; cf. Le Fèvre and Maramba, *J.*, 1952, 235), we made an upper estimate of μ 3·7—3·8 D for tropolone. Subsequent

measurements by Mills and Tyrell (*Chem. and Ind.*, 1951, 30) and Kubo, Nozoe, and Kurita (*Nature*, 1951, **167**, 688) agree with this. Moreover, according to the arguments of Walsh (*Ann. Reports*, 1947, **44**, 45) as μ_{CO} rises so ν_{CO} should fall. Conjugation of C=O and C=C in piperitone lowers ν_{CO} from 1706 cm.$^{-1}$ [now observed for menthone; compare 1714 cm.$^{-1}$ for *cyclo*hexanone (Hartwell, Richards, and Thompson, *J.*, 1948, 1436)] to 1666 cm.$^{-1}$ (see Figure); consequently at the outset we expected ν_{CO} for tropolones to be *ca.* 40 cm.$^{-1}$ lower than for diosphenol.

Purpurogallin (cf. Haworth *et al.*, *J.*, 1950, 1631) was the only tropolone derivative available to us (see Figure, bottom curve); as a solid it exhibited strong absorption at 1590 cm.$^{-1}$ and weaker absorption at 1627 cm.$^{-1}$. Although of lower intensity, the latter seems to be that due to carbonyl.

Since then, the various ν_{CO} reported for simpler tropolones have all lain between 1610 and 1630 cm.$^{-1}$ (Broomfield, *Chem. and Ind.*, 1951, 30; Koch, *J.*, 1951, 512; Haworth and Hobson, *ibid.*, p. 561; Scott and Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240). Such figures are reminiscent of those (1613—1639 cm.$^{-1}$) for *o*-hydroxyacetophenone and the "conjugated chelates" studied by Rasmussen *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 1068).

In the ultra-violet region (Beckman spectrophotometer, Model D.U.), our specimens of piperitone and diosphenol gave somewhat broad maxima: piperitone, *ca.* 320 mμ (log ε 1·7), *ca.* 235 mμ (log ε 4·24); diosphenol, *ca.* 273 (log ε 4·05). These are in reasonable accord with others in the literature: piperitone, $\lambda_{max.}$ 3191 (ε 49) (Lowry and Lishmund, *J.*, 1935, 1313) or 3210 Å (ε 54) and 2355, (ε 17,780) (Gillam, Lynas-Gray, Penfold, and Simonsen, *J.*, 1941, 60); diosphenol, $\lambda_{max.}$ 2680 (ε not quoted) (Mayer, *Atti R. Accad. Lincei*, 1914, **23**, 439), 2715 (ε 11,000) (Walker and Read, *J.*, 1934, 230), 2725 (ε 11,150) (Lowry and Lishmund, *loc. cit.*), and 2740 (ε 11,000) (Gillam *et al.*, *loc. cit.*).

Diosphenol therefore differs from tropolone in its ultra-violet absorption since Cook *et al.* (*J.*, 1951, 503) and Haworth and Hobson (*ibid.*, p. 561) find maxima for the latter at two regions, 228 and 237 mμ (log ε, *ca.* 4·4), and 320 and 351 mμ (log ε, *ca.* 3·8).

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NOTES.

507. *Ditellurium Decafluoride.*

By W. D. ENGLISH and J. W. DALE.

THE lower fluorides of tellurium are not well known, and there is doubt as to the existence of many of the reported compounds (see, *e.g.*, Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford Univ. Press, 1950, pp. 990, 991). Yost and Claussen (*J. Amer. Chem. Soc.*, 1933, **55**, 885) reported that a by-product from the direct fluorination of tellurium had a higher molecular weight (340) than tellurium hexafluoride (242). They did not obtain enough to investigate it adequately, but Yost and Russell ("Systematic Inorganic Chemistry," Prentice-Hall Inc., New York, 1944, pp. 295, 299) later stated that the compound was probably impure ditellurium decafluoride.*

We have obtained ditellurium decafluoride in yields of up to 20% from the direct fluorination of tellurium in the presence of calcium fluoride. This compound was similar to disulphur decafluoride (Denbigh and Whytlaw-Gray, *J.*, 1934, 1346) in most of its properties such as odour, toxicity, and chemical behaviour.

Ditellurium decafluoride is a colourless, heavy liquid of remarkable volatility. Though

* Since this paper was submitted, the existence of tellurium tetrafluoride has been confirmed by Junkins, Bernhardt, and Barber (*J. Amer. Chem. Soc.*, 1952, **74**, 5749).

it has a molecular weight of 445 it boils at 327° K, by far the highest ratio of molecular weight to boiling point of any compound known. Its physical properties are:

M. p. −34° to −33°. V. p. equation (−33° to 54°): $\log p_{\text{mm.}} = -2063/T + 9{\cdot}20$ (r.m.s. deviations: ±1°). B. p.: calc., 54°; obs., 53°/748 mm. Heat of evaporation at normal b. p. (calc.): 9440 cal./mole. Trouton constant: 28·8 cal. mole^{-1} deg.$^{-1}$.* n_D^{20} 1·298; $d_{25}^{25} = 2{\cdot}88$.

Ditellurium decafluoride is fairly stable and may be stored for several months without much decomposition. However, it slowly attacks glass. The vapour attacks organic stop-cock greases immediately, turning them black, and the liquid dissolves fluorinated stop-cock greases. It reacts with acetone, turning it brown, and releases iodine from acetone solutions of potassium iodide, as does sulphur decafluoride.

Distilled water, or 1, 5, or 20% aqueous sodium hydroxide, had no apparent effect on liquid ditellurium decafluoride during 18 hours. Sodium attacked the compound slowly and quietly; potassium reacted with it vigorously and with frequent small explosions; both reactions yielded an insoluble black powder (Te?).

The yield was affected by conditions as follows. (i) Dilution of the fluorine with nitrogen reduced the yield. (ii) Dilution of the tellurium with sodium fluoride instead of calcium fluoride prevented the production of ditellurium decafluoride. (iii) Increase in the ratio of calcium fluoride to tellurium from 4·5 : 1 to 6·25 : 1 increased the yield by one-fifth.

Experimental.—Apparatus. The apparatus in which the fluorination took place consisted of a pile of three copper trays, 9 × 25 cm., with hollow bottoms through which cold water circulated. The trays were enclosed in a copper box, 10 × 26 × 16 cm. Fluorine was introduced by means of a perforated ring over each tray. Products were removed from the end of the box by a manifold and were condensed in Pyrex traps cooled in liquid air.

Synthetic procedure. Tellurium (100 g., of particle size such that 90% passed a 250-mesh and 65% a 325-mesh sieve) was mixed with calcium fluoride (450 g.; 50% passing a 100-mesh sieve), and the mixture dried at 110° for 2 days. It was then placed in the trays. The cooling water was turned on and fluorine was passed through at 16 g./hr. The reaction was continued until large quantities of unchanged fluorine started to condense in the trap cooled in liquid air. Distillation of the product yielded 117 g. (62%) of tellurium hexafluoride, 25 g. (19%) of *ditellurium decafluoride* (Found: Te, 56·9; F, 42·5. Te_2F_{10} requires Te, 57·3; F, 42·7%), and 0·5 ml. of an unidentified yellow oil, b. p. 92°/480 mm. The decafluoride had a molecular weight of 450 by vapour density (Calc.: 445) and MR_D 28·7 (Calc.: 27·6, AR_D for tellurium being taken as 8·80, see Fajans and Joos, *Z. Physik*, 1924, **33**, 27).

Ditellurium decafluoride was not produced when sodium fluoride (of particle size as for tellurium, above) was used to dilute the tellurium.

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* Disulphur decafluoride has a Trouton constant of 23·0 (Denbigh and Whytlaw-Gray, *loc. cit.*) or, more probably, 20·2 (Hoffman, personal communication).

508. cyclo*Octatetraene Derivatives. Part II.* Condensation of* cyclo*Octatetraene with Phenol.*

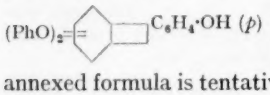
By William O. Jones.

The reaction between *cyclo*octatetraene and phenol has been examined; concentrated hydrochloric acid and boron trifluoride–acetic acid complex were good catalysts; stannous chloride, aluminium chloride, zinc chloride, and sulphuric acid were less effective. Phenol condensed with *cyclo*octatetraene in the molecular ratio of 3 : 1, and to ensure complete utilisation of the hydrocarbon, 4—6 mol. of phenol were used at 20—50°. Higher temperatures led to dark rubber-like products which became brittle on storage.

The normal product was a pale pink solid, melting indefinitely at 120—130°, which could not be satisfactorily crystallised even after chromatographic resolution. Distillation at 0·8 mm. appeared to cause structural changes in the product.

Methylation gave a colourless ether, m. p. 50—55°, which yielded a small amount of anisic acid on oxidation. The phenolic condensation product gave a derivative of phenoxyacetic acid by reaction with chloroacetic acid. Neither of these derivatives was sharp melting. The equivalent weight of the phenoxyacetic acid indicated that only one of the three phenol molecules had retained its hydroxyl group, the other two presumably being present as phenoxy-groups.

The phenol reacted rapidly with 8 mol. of chlorine, suggesting substitution in the phenoxy–groups (2 × 3) and the phenolic part (2). A trinitro–derivative was also made.



Because of the intractability of the phenolic condensation product and its derivatives, conclusive proof of its structure has not been obtained. To account for the present results the annexed formula is tentatively suggested as representing the type of compound produced.

o- and *p*-Chlorophenols and resorcinol have also been condensed with *cyclo*octatetraene.

Experimental.—Condensation product from cyclo*octatetraene and phenol.* *cyclo*Octatetraene (20·8 g.), phenol (113 g.), and concentrated hydrochloric acid (1 ml.) were stirred for 18 hours at room temperature, and the resulting viscous mixture was steam-distilled. The residue cooled to a pale pink brittle solid (62 g.; m. p. 125—130°). Amorphous material (Found: C, 78·1; H, 6·8%) was invariably obtained from all attempts at crystallisation. Chromatography on alumina gave only gummy products. In another experiment the product was distilled at 0·8 mm. Two fractions were collected, at 100—180° (orange) and at 180—230° (red), but the major portion could not be distilled. Both fractions melted at 25—30°, and they now formed brownish-red solutions (green fluorescence) in dilute sodium hydroxide, whereas before distillation such solutions were almost colourless.

At 70° a vigorous exothermic reaction occurred and the flask filled with a dark blue rubber-like material, which became brittle and was almost insoluble in dilute sodium hydroxide.

The condensation product (10 g.) was converted, by methyl sulphate, into its methyl ether (10 g.), m. p. 50—55°, which could not be obtained crystalline (Found: C, 79·8; H, 7·6%). The ether (5 g.) yielded anisic acid (0·5 g.; m. p. 182—184°; equiv., 160) when oxidised with potassium permanganate (20 g.) in boiling sodium carbonate solution (200 ml.; 5%).

An impure phenoxyacetic acid (m. p. 120—140°; equiv., 413) was prepared in the usual manner.

Dropwise addition of fuming nitric acid (11 g.) at 5—15° to a solution of the condensation product (19 g.) in acetic acid (200 ml.) gave a trinitro-derivative (25·5 g.). This was purified by passage of an aqueous solution of the sodium salt through alumina. The *derivative* was eventually obtained as a pale yellow powder (from chloroform), m. p. 140—150° (Found: C, 59·3; H, 4·6; N, 7·2. $C_{26}H_{23}N_3O_9$ requires C, 59·9; H, 4·4; N, 8·1%).

The rate of chlorination of the condensation product was determined at 20° by treating it (0·477 g.) with chlorine (10 mol.) in acetic acid (500 ml.) and removing samples (5 ml.) periodically for titration. 8 mol. of chlorine were absorbed in 3 min., at which point there was a sharp break in the time–titre curve.

Condensation products from cyclo*octatetraene and other phenols.* With *o*- and *p*-chlorophenol

* Part I, *J.*, 1953, 2036.

the reaction was carried out at 55° but for 10 hr. The crude mixtures did not thicken very much, and approximately 50% of the *cyclo*octatetraene was recovered. The *o*-isomer gave an alkali-soluble black product (m. p. 150—170°) whereas that from the *p*-isomer was dark brown (m. p. 60—70°) and was not soluble in alkali. To obtain adequate mixing, the reaction between resorcinol (270 g.) and *cyclo*octatetraene (52 g.) was carried out in acetic acid (200 ml.) at 20—28° in the presence of boron trifluoride–acetic acid (2·5 ml.). The residue obtained on steam-distillation consisted of an intense brownish-red solution, from which a solid (viscous at first, but brittle later; m. p. 165—200°; 63 g.) was obtained on acidification. The product was readily soluble in dilute sodium carbonate solution.

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509. 2 : 4 : 5-*Trimethyl* D-*Arabonamide*.

By P. W. KENT and M. W. WHITEHOUSE.

IN the demonstration of the ring structure of methylfuranosides of D-glucosamine, methylation and oxidation would be expected to lead to 2 : 4 : 5-trimethyl D-arabinose. This sugar has been obtained by the action of hypochlorite on 3 : 5 : 6-trimethyl D-gluconamide (Haworth, Peat, and Whetstone, *J.*, 1938, 1975) as a syrup having properties characteristic of an *aldehydo*-sugar, *viz.*, ready reaction with potassium permanganate and Fehling's solutions, and restoration of the colour to Schiff's reagent. No crystalline derivatives were reported. A recent re-examination (Dodgson and Pryde, *Nature*, 1952, **170**, 35) of the " trimethylarabinose " obtained in this way showed it to be a mixture of at least four substances which could be separated chromatographically: one fraction only had typical aldehydic properties and this corresponded to a dimethyl pentose; another contained nitrogen.

We have now prepared 2 : 4 : 5-trimethyl D-arabinose by direct oxidation of 3 : 5 : 6-trimethyl D-glucose by sodium metaperiodate. The initial trimethyl glucose (Anderson, Charlton, and Haworth, *J.*, 1929, 1329) was chromatographically homogeneous and yielded a syrupy but homogeneous trimethyl pentose which readily reduced Fehling's solution, restored the colour to Schiff's reagent, and had an absorption band at 2550—2650 Å comparable with that of penta-acetyl *aldehydo*glucose (Wolfrom, *J. Amer. Chem. Soc.*, 1929, **51**, 2188). Further oxidation with bromine gave the corresponding arabonic acid from which an ester and thence crystalline 2 : 4 : 5-trimethyl D-arabonamide were obtained. The amide gave a negative Weerman test.

Experimental.—Chromatographic constants were determined throughout on Whatman No. 1 paper in butanol–ethanol–water (4 : 1 : 5). R_G values refer to the ratio of the distance traversed by a sugar to that of 2 : 3 : 4 : 6-tetramethyl glucose, when investigated simultaneously.

2 : 4 : 5-*Trimethyl* D-*arabinose*. 3 : 5 : 6-Trimethyl D-glucose {0·9 g.; n_D^{20} 1·4660, $[\alpha]_D^{22}$ −9° (*c*, 1·8 in H_2O), R_G 0·86} and sodium metaperiodate tetrahydrate (1·35 g.) were dissolved in water (100 ml.). Trimethyl arabinose was detected chromatographically after 6 hr. at room temperature in darkness. After 24 hr. barium carbonate (5 g.) was added and the solution was extracted with chloroform and the dried extract was concentrated to a syrup from which the product was extracted with acetone. Cautious evaporation of the solvent gave syrupy 2 : 4 : 5-trimethyl D-arabinose (0·5 g.), n_D^{17} 1·4655, $[\alpha]_D^{20}$ +18·5° (*c*, 0·6 in $COMe_2$), R_G 0·96 (Found: OMe, 46·2. $C_8H_{16}O_5$ requires OMe, 48·2%).

Methyl (2 : 4 : 5-*trimethyl* D-*arabonate*). 2 : 4 : 5-Trimethyl D-arabinose (0·105 g.) in water (5 ml.) containing bromine (8 drops) was kept for 5 days, whereafter it had no reducing properties. Excess of bromine was removed by aeration and the solution neutralised with silver carbonate. The filtrate was saturated with hydrogen sulphide, and after refiltration and evaporation the resulting acid was esterified by boiling 1% methanolic hydrogen chloride for

5 hr. The solution, neutralised with silver carbonate and filtered, gave on evaporation *methyl* (**2 : 4 : 5-***trimethyl* D-*arabonate*), n_D^{17} 1·4438 (Found : OMe, 56·1. $C_9H_{18}O_6$ requires OMe, 56·1%).

2 : 4 : 5-*Trimethyl* D-*arabonamide*. The above ester, dissolved in dry saturated methanolic ammonia was kept at 0° for 24 hr. Removal of the solvent gave the *amide* which, recrystallised from acetone, had m. p. 144°, $[\alpha]_D^{21}$ −35·2° (*c*, 0·5 in EtOH), R_G 0·78 (Found : N, 6·5; OMe, 45·8. $C_8H_{17}O_5N$ requires N, 6·8; OMe, 45·0%) (cf. **2 : 3 : 5**-trimethyl D-arabonamide, m. p. 137—138° $[\alpha]_D^{19}$ −19° in MeOH, and **2 : 3 : 4**-trimethyl D-arabonamide, m. p. 96°, $[\alpha]_D^{20}$ −25° in MeOH).

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510. *The System* $Cr_2(SO_4)_3$–H_2SO_4–H_2O.

By Duncan Taylor.

In the system $Al_2(SO_4)_3$–H_2SO_4–H_2O, Taylor and Bassett (*J.*, 1952, 4431) have shown that, (*a*) as the acid concentration increases at 25° the solid phase $Al_2(SO_4)_3,16H_2O$ is followed by an unusual series of hydrated acid sulphates, (*b*) the 14-hydrate appears as a stable solid phase only at higher temperatures (50—60°), and (*c*) the anhydrous sulphate is not obtained except in concentrated acid solutions near the boiling point. In view of the well-known isomorphism of aluminium and chromic compounds, it was of interest to see if the same behaviour was observed in the corresponding chromic sulphate system, especially since in the latter there is a much stronger tendency for the formaton of complex co-ordination compounds. Furthermore, although extensive data are available regarding hydrated and acid sulphates of chromium (Mellor, " Inorganic and Theoretical Chemistry," Longmans, 1924, Vol. 11, p. 434), no systematic investigation of the ternary system appears to have been published previously.

From our work it is concluded that (*a*) chromium does not form a series of hydrated acid sulphates as does aluminium, and (*b*) many of the data in Mellor (*op. cit.*) regarding acid sulphates of chromium are unreliable.

Experimental.—Phase-equilibria data were obtained at 25° by using techniques very similar to those already described for the aluminium sulphate system, except that to obtain dry samples of the solid phases the wash liquid was methanol at low sulphuric acid concentrations and acetone containing 10% by volume of methanol at high acid concentrations. These wash-liquids caused no dissolution of the solid phases and no precipitation of solids from the appropriate saturated solutions. Several months' stirring were used in all cases to establish solid–liquid equilibrium. This was essential because it was frequently observed, particularly at low acid concentrations, that a solid phase may be precipitated but redissolved within a few days as the nature of the chromium co-ordination in the liquid phase changed.

Chromic sulphate (B.D.H.) was used as starting material without further purification; it was shown to contain slightly more than 16 molecules of water of crystallisation and had an *X*-ray powder photograph identical with that of solid A (see Table). Other reagents were " AnalaR " wherever possible.

Analytical procedure. All samples of liquid and solid phases, except the anhydrous sulphate, were analysed for total sulphate and chromium, water being determined by difference. Experiments with synthetic mixtures showed that total sulphate could be determined with an accuracy of a few parts in 1000 (low tendency rather than high) by titration with sodium hydroxide to a first end-point in the cold with phenolphthalein as indicator and then completing the titration at the b. p. These results were irrespective of the ratio $Cr_2(SO_4)_3 : H_2SO_4$ and of the total weight of chromium present. Chromium was determined by oxidation to the dichromate stage with ammonium persulphate (Vogel, " Quantitative Inorganic Analysis," Longmans Green & Co., 1948, p. 370). Anhydrous chromic sulphate could not be dissolved in water except in presence of chromous ions (cf. Sidgwick, " Chemical Elements and Their Compounds," Oxford, 1950, Vol. 2, p. 1013), and was analysed only for chromium by ignition to Cr_2O_3. Since the anhydrous phase was formed in boiling concentrated sulphuric acid, its water content was assumed to be less than 1·0% [cf. anhydrous $Al_2(SO_4)_3$].

Results. Analyses for all liquid and solid phases are given in the Table in compositions by weight. At 25° up to an acid concentration of about 10%, $Cr_2(SO_4)_3,16H_2O$ (A in the Table) is the stable solid phase and has an *X*-ray powder photograph identical with that of $Al_2(SO_4)_3,16H_2O$. The analytical values actually correspond more nearly to a 15-hydrate, but in view of the *X*-ray data, solid A must be the 16-hydrate. Between 10 and 30% of acid, a second form of the 16-hydrate (B in the Table) is obtained, and although the analytical values for A and B differ slightly, close similarity of *X*-ray powder photographs and identity of crystal habit (small violet elongated hexagonal plates) make it practically certain that the two have the same stoicheiometric composition and very similar geometrical configurations. In the range 30—45% of acid, the solid phase is the 14-hydrate (C in the Table). This was obtained only from solutions which initially were highly supersaturated, and occurs as minute, pale blue needles with a characteristic *X*-ray powder photograph. A tracer experiment with radiocæsium (cf. Taylor and Scott, *Nature*, 1951, **168**, 520) showed that phase C could not contain more that about 3% of sulphuric acid, and was therefore most unlikely to be an acid sulphate. Although no further solid phases could be obtained at higher acid concentrations even after 6 months' stirring, heating an approximately 5% chromic sulphate solution in concentrated

The system $Cr_2(SO_4)_3$–H_2SO_4–H_2O at 245°.

Solution		Dry solid phase			Solution		Dry solid phase		
$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase	$Cr_2(SO_4)_3$, %	H_2SO_4, %	$Cr_2(SO_4)_3$, %	H_2SO_4, %	Solid phase
39·05	0·0	58·77	0·0	A	13·52	31·08	38·45 *	13·39 *	B
—	—	59·45	0·0	A	8·48	38·26	27·41 *	24·05 *	C
30·80	7·06	58·80	0·83	A	7·31	43·21	60·71	0·78	C
26·51	11·68	59·83	0·0	B	—	—	60·31	0·49	C
23·15	15·90	59·40	0·0	B	—	—	60·62	1·08	C
19·70	20·73	—	—	B	—	—	81·9 †	~18	Anhyd.
17·10	24·27	60·4	0·17	B	—	—	82·6 †	~17	Anhyd.

* Moist solid phase. † Temperature ~300°.

Solid phases: A and B = two forms of $Cr_2(SO_4)_3,16H_2O$ [Calc.: $Cr_2(SO_4)_3$ = 57·6%].
C = $Cr_2(SO_4)_3,14H_2O$ [Calc.: $Cr_2(SO_4)_3$ = 60·9%].

acid to the b. p. readily gave the anhydrous sulphate as a salmon-pink microcrystalline solid, whose *X*-ray powder photograph showed exactly the same pattern of spacings as that of anhydrous aluminium sulphate, the absolute values of the spacings being a few units % greater. The solid probably contains considerably more intercrystallite sulphuric acid than the corresponding aluminium compound. Also, a series of solid solutions of composition $(Al,Cr)_2(SO_4)_3,H_2SO_4,2H_2O$ was obtained by heating mixtures of aluminium and chromic sulphates in 80% sulphuric acid till fuming commenced. Each member of the series gave an *X*-ray powder photograph identical with that of the parent aluminium compound, but the crystal habit was quite different: small pale green needles (colour deepening with chromium content) instead of colourless regular hexagonal plates. With a molecular ratio $Cr_2(SO_4)_3 : Al_2(SO_4)_3 = 9$ in the liquid phase, the precipitated solid solution contained not more than 3 atoms of chromium to every 7 of aluminium, and it therefore appears unlikely that a pure chromium 1,1,2 compound could be prepared. Attempts to prepare acid chromic sulphates by adding "AnalaR" acetone to solutions containing about 10% of $Cr_2(SO_4)_3$ and 75—90% of H_2SO_4, and which had been stirred previously at 25° for several months, gave green, exceedingly deliquescent precipitates. These contained only 2—3% of free acid, and by *X*-ray powder photographs were shown to be amorphous. Apart from the 1,1,2 solid solutions, these were the only green solid phases encountered in this work; on the other hand, all saturated liquid phases were deep green.

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511. *The Methoxyl Content of Gum Tragacanth.*

By KEITH SELBY.

GUM TRAGACANTH, an exudation of shrubs of the genus *Astralagus*, has been claimed by James and Smith (*J.*, 1945, 739) to contain "methoxyl groups (OMe, 3·8%) of an etheric nature since the methoxyl content was unchanged by treatment of the gum with sodium hydroxide solution." Recent work in these laboratories has shown, however, that a portion of the uronic acids is esterified in the natural gum and that virtually the whole of the methoxyl content occurs in the form of methyl ester.

The evidence for this conclusion is based on changes in carboxyl and methoxyl contents of alkaline solutions of the gum on storage in the cold. In a typical experiment a sample of "medium flake" gum tragacanth (60 g.) was fractionated by dissolution in a dilute buffer solution [10^{-4}M-sodium acetate and $0{\cdot}4 \times 10^{-4}$M-acetic acid] (10 l.). After several days in the refrigerator the swollen but undissolved material, bassorin, was removed by centrifugation and the soluble fraction, tragacanthin, was isolated (30 g.). This material (OMe, 3·38%; 0·5 g.) was allowed to react in solution (50 ml.) with potassium hydroxide (2·41 milliequiv.) at room temperature for periods of ½ to 72 hr. The carboxyl content of each sample was then determined by titration to pH 8. The solutions were immediately readjusted to the pH value of the natural gum and, after evaporation *in vacuo* with successive small quantities of water to remove any volatile alcohols, the methoxyl contents were determined by a semimicro-modification of the Zeisel method (Samsel and McHard, *Ind. Eng. Chem. Anal.*, 1942, **14**, 750) (see Table). Similar experiments with bassorin (OMe, 1·03%) and with the whole gum, as well as with samples of pharmaceutical quality (OMe, 2·00%), gave similar results.

Change (milliequiv./g. of gum) in carboxyl and methoxyl contents of tragacanthin during saponification.

Time (hr.)	CO_2H	OMe	Gain in CO_2H	Loss of OMe	Time (hr.)	CO_2H	OMe	Gain in CO_2H	Loss of OMe
0	0·26	1·08	—	—	2	1·16	0·22	0·90	0·86
½	0·78	0·44	0·52	0·64	72	1·37	0·04	1·11	1·04

It was established that no part of these changes was due to atmospheric oxidation. The viscosities of the solutions were unchanged during the saponification, showing that polymeric ester linkages were not involved. The close relation between gain in carboxyl content and loss of methoxyl content suggested that the change taking place was hydrolysis of methyl ester groups.

For confirmation of the production of methanol during saponification of tragacanthin, volatile alcohols produced were concentrated by fractional distillation. Oxidation with acidic potassium permanganate (Hoffpauir and Reeves, *Analyt. Chem.*, 1949, **21**, 815) yielded formaldehyde, characterised as its dimedone derivative, m. p. and mixed m. p. 190°.

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512. 1 : 2-O-iso*Propylidene*-β-D-*altrofuranose.*

By F. H. NEWTH.

THE partial hydrolysis of 1 : 2-5 : 6-di-*O*-*iso*propylidene-α-D-glucofuranose under mildly acidic conditions to give 1 : 2-*O*-*iso*propylidene-α-D-glucofuranose is well known. The analogous reaction in the D-altrose series is now described. 1 : 2-5 : 6-Di-*O*-*iso*propylidene-β-D-altrofuranose (Steiger and Reichstein, *Helv. Chim. Acta*, 1936, **19**, 1011; Newth and Wiggins, *J.*, 1950, 1734), when treated with 80% acetic acid, lost one *iso*propylidene residue, and 1 : 2-*O*-*iso*propylidene-β-D-altrofuranose was formed in excellent yield.

Steiger and Reichstein assigned the *iso*propylidene residues to positions 1 : 2 and 5 : 6 in the D-altrofuranose molecule on the basis of steric considerations and the fact that the compound was not oxidised by permanganate. It is now possible to provide a more definite proof of its constitution. 1 : 2-5 : 6-Di-*O-iso*propylidene-β-D-altrofuranose formed a crystalline 3-*O*-toluene-*p*-sulphonate which failed to react with sodium iodide in acetone at 110°. This clear indication of the absence of a primary tosyloxy group is consistent with the resistance of the di-*O-iso*propylidene compound to oxidation. Furthermore, 3-*O*-methyl-1 : 2-5 : 6-di-*O-iso*propylidene-β-D-altrofuranose could also be selectively hydrolysed to 3-*O*-methyl-1 : 2-*O-iso*propylidene-β-D-altrofuranose; this reacted with one mol. of lead tetra-acetate, and one mol. of formaldehyde was liberated. The oxidisable glycol system must, therefore, be at $C_{(5)}$–$C_{(6)}$, the situation of the more labile *iso*propylidene residue. The other residue is certainly joined to $C_{(1)}$ since all the above compounds are non-reducing and there is little reason to suppose that it is a 1 : 3- rather than a 1 : 2-*O-iso*propylidene group.

Experimental.—**1 : 2-O-iso*Propylidene*-β-D-*altrofuranose.*** A solution of **1 : 2-5 : 6-di-*O-iso*-propylidene-β-D-altrofuranose** (0·90 g.) in 80% acetic acid (20 ml.) was kept for 24 hr. and then evaporated to dryness at 65°. The residue was recrystallised from ethyl acetate, and **1 : 2-O-iso*propylidene*-β-D-*altrofuranose*** was obtained as small cubes (0·65 g.), m. p. 125—126°, $[\alpha]_D^{17}$ +25·8° (*c*, 1·01 in MeOH) (Found : C, 48·8; H, 7·1. $C_9H_{16}O_6$ requires C, 49·1; H, 7·3%).

1 : 2-5 : 6-*Di*-O-iso*propylidene*-3-O-*tosyl*-β-D-*altrofuranose.* The di-*O-iso*propylidene compound (0·10 g.) was treated with toluene-*p*-sulphonyl chloride in pyridine solution. The 3-O-*tosyl* derivative had m. p. 100—101° (from alcohol), $[\alpha]_D^{20}$ +30·7° (*c*, 0·85 in $CHCl_3$) (Found : C, 54·9; H, 6·4. $C_{19}H_{24}O_8S$ requires C, 55·0; H, 6·3%). The compound was recovered quantitatively after 16 hr.' heating with sodium iodide in acetone solution at 110°. In one instance this derivative (4 g.) separated from the mixture of di-*O-iso*propylidene-*O*-tosyl-D-altrose compounds [syrup *B*] obtained from a D-altrose–1 : 6-anhydro-β-D-altropyranose mixture (25 g.) (Newth and Wiggins, *loc. cit.*).

Reduction of **1 : 2-5 : 6-*di*-O-iso*propylidene*-3-O-*tosyl*-β-D-*altrofuranose with sodium amalgam.*** The compound (3·0 g.) was dissolved in 90% methanol (100 ml.), and sodium amalgam (3%, 60 g.) added. After being stirred overnight, the solution was decanted from the mercury, which was washed with methanol, and the combined solution and washings neutralised with carbon dioxide. The residue which was obtained when the solution was evaporated was extracted with chloroform. Evaporation of this extract provided **1 : 2-5 : 6-di-*O-iso*propylidene-β-D-altrofuranose** (1·6 g.), m. p. 87—88° after 3 recrystallisations from ether–light petroleum.

3-O-*Methyl*-1 : 2-5 : 6-*di*-O-iso*propylidene*-β-D-*altrofuranose.* **1 : 2-5 : 6-Di-*O-iso*propylidene-β-D-altrofuranose** (0·65 g.) was thrice treated with methyl iodide and silver oxide at 45°. The 3-O-*methyl* derivative (0·60 g.) distilled at 102° (bath)/0·05 mm. and had n_D^{23} 1·4499, $[\alpha]_D^{23}$ +4·0° (*c*, 1·24 in $CHCl_3$) (Found : C, 56·6; H, 7·8; OMe, 10·8. $C_{13}H_{22}O_6$ requires C, 56·9; H, 8·1; OMe, 11·3%).

3-O-*Methyl*-1 : 2-O-iso*propylidene*-β-D-*altrofuranose.* A solution of the above 3-*O*-methyl derivative (0·31 g.) in 80% acetic acid (10 ml.) was kept for 24 hr. and then evaporated at 65°. The syrupy residue distilled at 145° (bath)/0·04 mm.; the **3-O-*methyl*-1 : 2-O-iso*propylidene*-β-D-*altrofuranose*** (0·22 g.) had n_D^{17} 1·4734, $[\alpha]_D^{18}$ +10·2° (*c*, 0·39 in MeOH) (Found : C, 51·1; H, 7·5. $C_{10}H_{18}O_6$ requires C, 51·3; H, 7·7%). The compound consumed 0·955 mol. of lead tetra-acetate (5·3 hr.; 1·105 mol. after 20 hr.) under standard conditions. Formaldehyde (0·95 mol.), estimated as the dimedone derivative, m. p. 188—189°, was liberated during the reaction.

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OBITUARY NOTICES.

WILDER DWIGHT BANCROFT.

1867—1953.

In 1632, twelve years after the *Mayflower* sailed from Southampton and during the period of the "Great Migration," John Bancroft, accompanied by his wife and two young sons, left his English home in Norfolk to take a farm near Lynn, in the colony of Massachusetts. Although he died soon after, his son Thomas became the progenitor of a long line of stalwart churchmen and farmers; and, during more than a hundred and thirty years, five generations of Bancrofts developed a tradition and pattern of life which, as it has been said, "combined civic duties, rock-ribbed Calvinism and farming in equal proportions."

This seemingly settled and unchanging pattern and way of life, however, was shattered when, in November 1755, a son, Aaron, was born to Samuel Bancroft, farmer and deacon of the church in Reading, Massachusetts, and his wife Lydia Parker. Looked upon, even as a boy, as the "family rebel," Aaron liked neither the occupation nor the Calvinistic creed of his father, and, breaking with long-established tradition, he became a prominent Unitarian minister, a leader of the schismatics and a soldier of the Revolution. He also wrote a "Life of George Washington," which enjoyed considerable popularity; and it was his constant prayer that he might be granted a "teachable temper."

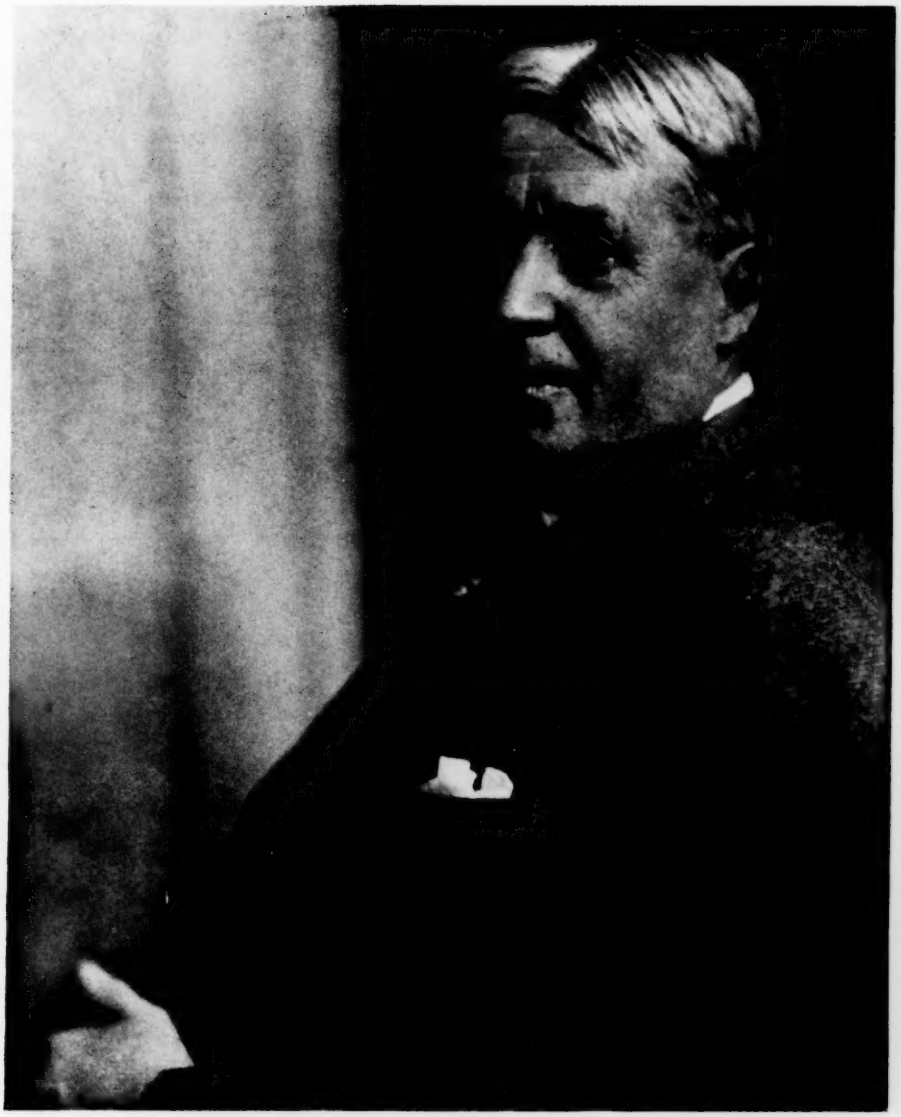
The character and cultural mutation introduced by Aaron into the Bancroft line was continued and confirmed in his son George: scholar, politician and diplomat; Secretary of the Navy under President Polk and founder of the U.S. Naval Academy at Annapolis; U.S. Minister in London and in Berlin; author of "History of the American Revolution" and of "History of the Formation of the Constitution of the United States of America." By his first wife, Sarah H. Dwight, he had two sons and a daughter; and the elder son, John Chandler, named after his grandmother, Lucretia Chandler, wife of Aaron Bancroft, became the father of Wilder. It is, I believe, in the mental qualities, outlook on life, personality, and character of his grandfather and great-grandfather, that we can find the key to the personality and character of the subject of this notice.

Wilder Dwight Bancroft was born on October 1st, 1867, at Middletown, Rhode Island, a small town and residential suburb of Newport, R.I. He was the elder of two children whom his father had by his first wife, Louisa Denny, daughter of a mill-owner, who died when Wilder was only four years old. Bancroft's father had studied law and was associated for a time with a firm of stockbrokers in Boston, but he later devoted himself to painting and studied art in France. His love of art, however, did not pass to his son. As a boy, Bancroft attended Roxbury Latin School and Milton Academy, where he showed outstanding ability, but little is known of his special interests or aptitudes during that period of his life. It was not, apparently, until he became an undergraduate at Harvard University in 1884 that any particular interest in science began to develop.

At that time, the senior professor of chemistry at Harvard was Josiah P. Cooke, whose books, "The New Chemistry" and "First Principles of Chemical Philosophy," may entitle him to be regarded as a pioneer of the older physical chemistry, and whose deductive method of approach to the study of chemistry cannot but have exercised an important influence on Bancroft's mind. There is little known about Bancroft's interests in science while at Harvard, but he showed prowess on the football field and was a member of the Harvard football team.

On graduating A.B. in 1888, Bancroft was appointed an Assistant in the Chemistry Department. In the following year he proceeded to Europe where he worked more especially under Wilhelm Ostwald in Leipzig (1890—2), and under van't Hoff in Amsterdam (1892—3). He also spent some time at Strasbourg (1889—90) and in Berlin. In 1892 he presented a thesis entitled "Oxydationsketten" and after the usual oral examination was awarded the degree of Ph.D. by the University of Leipzig. In Amsterdam he continued his electrochemical studies and carried out experiments of an exploratory character on the chemical potential of metals.

On returning to America in 1893, Bancroft took up his former post as Assistant at Harvard and in the following year was promoted to the rank of Instructor. In 1895 Professor Cooke died and Bancroft left Harvard to join the staff at Cornell University as Assistant Professor of Physical Chemistry. In 1903 he became Professor and, in 1919, World War Memorial Professor of Physical Chemistry. Thereafter the whole of his life was spent at Cornell. In



Wilder D. Bancroft

[To face p. 2506.

1937 he retired from his Chair, and for a year was visiting Tallman Professor at Bowdoin College, Brunswick, Maine.

For more than forty years Bancroft was a member of the staff of Cornell. They were very strenuous years, but years which were full of work in which he could find satisfaction and happiness; and as time passed he became one of Cornell's best known and most outstanding professors. As a teacher he sought to impress on his students something of his own high character and enthusiasm for scientific truth. He lectured interestingly and clearly, using the original memoirs as the basis of discussion. His aim was not so much to impart a knowledge of a large number of facts as to impress on his students the importance of thinking things out for themselves; and he assessed the merits and standing of a student not by the range or number of facts which he was able to commit to memory, but by his willingness and ability to think and to draw his own conclusions from the facts discovered by himself or by others. To make people think may, perhaps, be regarded as a major aim of Bancroft's many writings, and the success with which he achieved this aim may be reckoned as among the most important of his contributions to the advancement of physical chemistry in America.

To younger chemists in whom he detected merit, Bancroft gave much help and encouragement, and there are not a few who have since attained to positions of eminence in chemistry, who look back with gratitude to the stimulus, encouragement, and help which they received from him.

Bancroft was interested in teaching, in making known to others what he had learned himself. He was obsessed with the importance of chemistry and he strove to make its importance more widely known and appreciated. " It should be the aim of all chemists," he wrote in the Jubilee volume of the *Journal of the American Chemical Society*, " to have chemistry take its place as the fundamental science," and he also urged physical chemists " to develop the borderlands between physical chemistry and the other sciences, such as, biology, geology, physics, medicine, engineering, psychology, etc." Nor was it on his students and fellow-scientists alone that he wished to press the importance of chemistry. Its importance must be recognised by the community as a whole, and he suggested that universities should teach chemistry as a cultural study—as part of a general education. He urged, also, the institution of courses of public popular lectures on chemistry for those not to be chemists—" chemistry of or pertaining to all the people "—pandemic chemistry, he called it. Bancroft drew up a syllabus of such a course, a course not to teach a man chemistry but to teach him about chemistry, but he recognised, as all teachers have recognised, that the success of such a course depends more on the teacher than on the syllabus.

Bancroft was himself endowed with the gift of popular exposition, as shown by his lecture on " Blue Eyes and Blue Feathers " with which he gave pleasure to many audiences. Blue eyes, like the blue of the sky or of skimmed milk, are due to the Tyndall effect in turbid media; but the blue eyes of infants may change to hazel or brown through the development of a pigment in the front of the iris. Green eyes, due to a combination of structural blue with a yellow pigment, are " not common in human beings, except as a symbol of jealousy." The green colour on the back of the green tree-frog has a similar origin. " If we scrape the pigment layer off the back of an unfortunate frog, he turns blue." Blue and iridescent colours of feathers are due not to pigments but to physical structure. The lecture was a good example of Bancroft's happy lecture style; and the way in which apparently unrelated phenomena were brought together was characteristic of Bancroft's highly perceptive mind.

In 1895, physical chemistry—the newer physical chemistry of which Arrhenius, van't Hoff, and Ostwald were the pioneers—was only in its infancy in America, and Bancroft, with boundless energy and full of missionary zeal, sought, on joining the staff at Cornell, to develop this branch of science. In his view, physical chemistry was not merely a branch of chemistry but covered the whole of chemistry, and he aimed at presenting the science as a complete and systematic whole.

While in Amsterdam, Bancroft had no doubt become acquainted with the work of Bakhuis Roozeboom and had become impressed with the importance of the phase rule as a basis of classification of heterogeneous systems and as a guide in their investigation. Although it owed its discovery to the great Yale mathematician, Willard Gibbs, there was, in America, almost no knowledge of the great generalisation or recognition of its practical importance. There was, moreover, no exposition in English by means of which the student could become acquainted with it. Bancroft, therefore, set himself the task of making good this deficiency and published his first book, " The Phase Rule," in 1897. In this work, at the cost of what must have been much labour, he collected together in a systematic manner the existing items of knowledge scattered throughout the literature, and was, as Bakhuis Roozeboom wrote, " exceedingly

successful in making clear the coherence of the phenomena and in presenting an inspiring picture of the imposing science of heterogeneous equilibria." Unfortunately he was not quite successful, as he himself admitted, in producing a book which a student could read with profit and without difficulty. Nevertheless, it was a remarkable work to be written by one who was under thirty years of age and still on the very threshold of his teaching career. Along with the many papers written by Bancroft and the experimental work carried out by his pupils under his inspiration and guidance, "The Phase Rule" constituted a very important pioneering advance into a domain which, later, was vigorously and fruitfully cultivated in America. As Bancroft pointed out, the renowned Geophysical Laboratory at Washington is a wonderful example of what can be done with the phase rule as an instrument of research.

It is, perhaps, worthy of note that Bancroft, in this book, introduced into phase rule terminology the words non-variant, monovariant, divariant, etc., suggested to him by his colleague, Joseph E. Trevor.

In his desire to further the study of physical chemistry in America, Bancroft no doubt recognised, as Ostwald in Germany had recognised, that if this new branch of science was to grow and develop, it must have a special organ through which it could express itself, and so, in 1896, he founded *The Journal of Physical Chemistry* as "an organ for the publication of research in all branches of experimental and theoretical physical chemistry." Until 1932, Bancroft was editor of the *Journal* (associated during the first thirteen years with J. E. Trevor), contributed many articles to its pages, and wrote also for it many book reviews and abstracts of scientific papers published elsewhere. Not only did Bancroft found the *Journal of Physical Chemistry* and thereby, it may be, rendered his greatest service to chemistry, but he also financed it out of his private resources. In 1924, when the financial burden became too great for him, he handed the Journal over the the American Chemical Society, the Chemical Society, and the Faraday Society, under whose auspices it was published until 1932. In 1947 its title was altered to *Journal of Physical and Colloid Chemistry*. It would be impossible with any accuracy to assess, as it would be difficult to exaggerate, the value and importance of this journal in promoting the development of physical chemistry in America by uniting the workers in this new domain of knowledge, by giving them their own organ of publication and thereby making effective advance possible.

From 1913 until his death, Bancroft was also Associate Editor of the *Journal of the Franklin Institute*, an institute founded, in 1826, in the State of Pennsylvania, to "diffuse information on every subject connected with the useful arts." To this journal Bancroft contributed, in 1925, an article on the Development of Colloid Chemistry.

The numerous papers on emulsions, colloids, adsorption, etc., which from just before the First World War appeared in the *Journal of Physical Chemistry* under the name of Bancroft and of his pupils, were evidence that a new interest, one which became, perhaps, his strongest and most enduring interest, had developed in Bancroft's mind.

For some time interest in the colloid state had been growing in America, as in Europe, and although books on colloid chemistry existed, they had been written, in Bancroft's opinion, in too purely descriptive a manner and presented the subject empirically. By 1920, he considered that theory had developed sufficiently to allow the data to be presented deductively, and this he sought to do in his "Applied Colloid Chemistry," which first appeared in 1921 and of which two further editions were published, in 1926 and 1932.

This book, in its enthusiastic presentation of the subject, its critical sifting of reputed facts and explanations which the author regarded as doubtful or conflicting, its stimulating suggestiveness of how information gained in one field of investigation may be applied in many other fields, is entirely characteristic of Bancroft and deals clearly and comprehensively with a wide range of facts and observations. It is a book which is not only interesting and easy to read, but is sometimes almost entertaining, as when Bancroft writes: "There is one experiment which I always like to try, because it proves something whichever way it goes. A solution of iodine in water is shaken with bone-black, filtered, and tested with starch paste. If the colourless solution does not turn starch blue, the experiment shows how completely charcoal extracts iodine from aqueous solution. If the starch turns blue, the experiment shows that the solution, though apparently colourless, still contains iodine which can be detected by means of the sensitive starch test." One can almost see the engaging twinkle in his eyes as he carries out this experiment in front of his class.

The title of the book shows that Bancroft was interested not only in the general theory of colloid matter, but also in the importance of colloids and colloid theory in industry. To quote the author's own words: "At first sight colloid chemistry may not seem to be an important

branch of chemistry, either theoretically or technically; but this opinion changes when we consider that a knowledge of colloid chemistry is essential to anybody who really wishes to understand about: cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soap, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, celluloid, and other plastics; leather, paper, textiles; filaments, casts, pencils, and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines; zinc, phosphorus, sodium, and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale, and wine; cream, butter, cheese, and casein products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacology, physiology, and medicine. In other words, colloid chemistry is the chemistry of everyday life. It now looks as though insanity were primarily a problem in colloid chemistry."

A committee on the chemistry of colloids, of which Bancroft was a member, was set up in 1921 by the National Research Council. A National Symposium on Colloid Chemistry was held at Madison, Wis., in 1923, and thereafter became an annual event. At the 8th Annual Colloid Symposium the chemistry of anæsthesia, a problem in which Bancroft was directly interested and to the study of which he made valuable contributions, was discussed; and a Testimonial Dinner was arranged in his honour. In 1941, the 18th Annual Symposium, held at Cornell University, which was one of the first American Universities to institute courses in colloid chemistry, was designated " The Wilder D. Bancroft Symposium," " in recognition of his position as a pioneer among the teachers and investigators of colloid chemical phenomena in America and of his contributions to colloid science."

Although Bancroft was the author of only two books, writing, with him, may almost be said to have been an inherited characteristic, and he wielded the pen with ease and dexterity. He was an omnivorous reader and a voluminous writer, living constantly under the urge not only to seek out truth but to proclaim to others the truth when found. He had a wonderfully retentive memory and was a great encyclopaedist. In the many papers which he published in the *Journal of Physical Chemistry* and elsewhere, and in the numerous lectures and addresses which he delivered, Bancroft sought to bring together the facts already known, to sift them carefully and critically, to point out what he regarded as errors or defects in the interpretation of experimental data, to indicate what, in his opinion, were the fundamental problems to be investigated, and to put forward generalisations for testing by experiment. Ideas, suggestions of problems for investigation, sprang in almost bewildering profusion out of an extensive knowledge and exuberant imagination; and not a few of these problems were thereafter investigated by Bancroft's pupils in his laboratory at Cornell and under his stimulus and direction. It is, I believe, in his numerous writings and in the stimulus and encouragement which he gave to workers in widely different fields to take the data and conceptions from one branch of study and to consider their application to another, that we find Bancroft's chief contribution to the advance of scientific thought and knowledge.

Tall and strongly built, robust both physically and mentally and with a fair and fresh complexion, Bancroft looked out on a world which was to him so full of interest, through blue eyes from which a smile was never far distant. Throughout most of his life he retained as a spectator an enthusiastic interest in athletics, especially baseball and football, in which, in his younger days, he had gained no little distinction. Independent, as always, of the opinions of others, Bancroft was also inclined to be unconventional in dress. Van't Hoff tells how, during a visit which he paid to Bancroft in 1901, he was surprised to see his host dressed in knickerbockers and shoes, and how he reminded him somewhat of an *impressario*. He recounts, also, a somewhat hair-raising excursion to Taughannock Waterfall which he and his wife made in a horse carriage with Bancroft as driver. By some mistake they had got on to a road long disused and they had to descend and push or pull the carriage over the roughest parts, or even to lift it over a water conduit. However, they all arrived back again without serious mishap, and van't Hoff committed his feeling of relief to his diary in the words, " How fortunate we were to have such a safe driver as Wilder."

Bancroft found relaxation mainly in playing golf, and he was one of the organisers of the Country Club at Ithaca. He greatly enjoyed taking part in national and international congresses and conferences where he could discuss scientific problems with fellow workers. On such occasions, his genial and enthusiastic manner and his witty talk ensured for him a cordial welcome.

Bancroft was ambidextrous and, when lecturing, he liked sometimes to astonish and impress his audience by a demonstration of his ambidexterity. Standing at the middle of the blackboard he would begin to write a line with his left hand and then, transferring the chalk but without altering his position, would complete the line with his right hand.

Bancroft's eminence in science and his sound judgment in administrative matters were recognised both nationally and internationally. In 1905, and again in 1919, he was elected President of the American Electrochemical Society, in the foundation of which, in 1902, he had played an important part and of which he had been one of the first vice-presidents; and in 1910 he had the high honour bestowed upon him of being called to the Presidency of the American Chemical Society. He was also elected a member of the National Academy of Sciences. Other honours came to him both from within and without the United States. The Chemical Society elected him to Honorary Fellowship in 1920, and a similar honour was conferred upon him by the Polish Chemical Society and by the Société Chimique de France. Lafayette College conferred on him the honorary degree of Doctor of Science (1919), and the University of Southern California conferred the degree of Doctor of Laws (1930). On the occasion of the meeting of the International Congress in 1923, the honorary degree of Doctor of Science was conferred upon him by the University of Cambridge. On this occasion, the Public Orator presented him to the Vice-Chancellor with the words: Sequitur Wilder D. Bancroft et studiis et affinitate nobis conjunctus, qui alter Ulixes multorum providus, novam Ithacam novis artibus illuminavit.

During World War I, Bancroft was a member of the Advisory Committee, Chemical Warfare Service, and from 1918—19 had the rank of Lieutenant-Colonel. He was, very appropriately, in charge of the editorial section of the Chemical Warfare Service and had to deal with all reports coming in from various sections with reference to the preparation and properties of war gases. On the basis of these reports and of information collected from all available sources, monographs relating to each poison gas, to canister ingredients, etc., were compiled and made available to all interested in these matters.

For the year 1919—20, Bancroft was Chairman of the Division of Chemistry, National Research Council, and in that capacity wrote a Report in which he outlined a number of borderland problems which interested him and which he thought worth investigating. They included a wide range of subjects, from the bread-making quality of flour to tapping trees for turpentine and rubber; from chemotherapy to structural colours; from plasticity of clay to adsorption of gases; a range of topics which sufficiently indicates the catholicity of Bancroft's interests.

From 1922 to 1923, Bancroft was Vice-President of the International Union of Chemistry; from 1922 to 1925 a member of the Board of Visitors, Bureau of Standards; and in 1928 a member of the Advisory Board, Cancer Research Fund.

On June 19th, 1895, Bancroft married Kate Bott, of Albany, N.Y., whose father had emigrated from Germany to the United States about the middle of the nineteenth century, and whom he had first met during his period of study in Berlin in 1893. She died in February, 1942.

In 1937, when Bancroft retired from the active work of his Chair, he was still in the enjoyment of good health and could look forward to spending the evening of a very busy life in the unhurried, happy, and peaceful pursuit of his scientific interests. But this was not to be. In 1938, after returning from Bowdoin College, he was run over by a motor car on the Cornell Campus and received very severe injuries. For several months he lay in hospital and, although, thereafter, he was able to move about quietly with the help of a walking-stick and to pay occasional visits to the Chemistry Department, he never fully recovered his health. A year or two before he died he fell out of bed during another period in hospital and was then confined to his home.

During his many years of partial or complete invalidism Bancroft, undaunted by the cruel rub of fortune, remained cheerful and retained his interest in science and athletics; and smiling into the frowning face of Fate, he fulfilled his allotted span of life. Peacefully, on the morning of February 7th, 1953, he fell on sleep.

Bancroft is survived by two sons and three daughters, of whom the eldest is married to M. L. Nichols, Professor of Chemistry, Cornell University.

With his alert and wide-ranging mind, with his independence of outlook and fearlessness in expressing his views, which were in no way inferior to those of his New England forebears, Bancroft was an outstanding personality and exercised a great influence on the development of physical chemistry in America. It may be that in his editorial chair Bancroft was apt to regard himself not only as the professor but also as the autocrat of physical chemistry; it may also be that with his unusually wide knowledge and confidence—not unjustified—in his own judgment, he was inclined to be intolerant of the views of others when they differed from his own and to express his criticisms not only freely but, occasionally, with an unnecessary acerbity of language, and so was apt to make personal enemies of those who, through association in work and community of interests, should have been his friends. If, in the interests of scientific truth, he provoked controversy; if sometimes he even seemed, almost wilfully, to revert to

the character of his grandfather, " the aggressive partisan who appeared to court unpopularity," yet in the social relations of everyday life how considerate and lovable he could be, how gracious and charming his manner, how interesting and entertaining his conversation. He died leaving a wealth of achievement as his monument and a treasured memory that will not quickly fade.

Bancroft's scientific interests were very varied and evidence of his encyclopaedic mind is given in the numerous papers and articles which he wrote on electrochemistry, oxidation–reduction cells, and overvoltage; phase rule; osmotic pressure and dilution law; contact catalysis; corrosion; colloids and emulsions; hydrogenation; charcoal; theory of photography and the photographic plate; photochemistry; structural colours; proteins; colouring of glass by metal oxides; etc. To discuss here his scientific contributions in detail, would be impossible; and one must restrict oneself to indicating only some of the more important aspects of his scientific work.

The first investigations which Bancroft undertook after graduating at Harvard were electrochemical. In Ostwald's laboratory in Leipzig he carried out a large number of determinations of the electromotive force of cells in which unattackable electrodes were placed, one in a solution of a reducing agent and the other in a solution of an oxidising agent, the two solutions being connected by a salt bridge. This investigation had been suggested by Ostwald who recognised the importance of such cells in enabling one to calculate the chemical affinity of oxidation and reduction processes; and Bancroft was the first to carry out a large series of such determinations. The work gave evidence of Bancroft's experimental skill, but the value of the results was diminished because it was not realised or recognised that, as Le Blanc first pointed out, the electrode potentials are well-defined only when the solution contains both oxidant and reductant, and vary with the ratio of the concentrations or activities of these in the solution.

Pioneer determinations of the potential of irreversible electrodes were also carried out by Bancroft and his pupils at Cornell University, and this work was extended to the investigation of a number of cells with the object of finding a convenient standard cell with an e.m.f. of about 0·5 v.

The more practical applications of electrochemistry to the deposition of metals also claimed Bancroft's interest, and he showed that the crystal size of the deposited metal is decreased when there are present at the cathode surface substances which are adsorbed by the deposited metal. Thus, by the addition of suitable organic substances of high molecular weight to the cathode solution, smoother and finer-grained deposits could be obtained.

A process for the electrodeposition of chromium on steel, from a solution of chromic acid to which a small amount of chromium sulphate had been added, was worked out by Bancroft and his pupils. Further investigation of the process was, however, abandoned as the primary object of the investigation, the obtaining of a chrome steel, was not attained.

Overvoltage, the occurrence of which is of importance in the electrolytic reduction of both inorganic and organic compounds, was considered by Bancroft to be due to the formation of monoatomic hydrogen followed by the combination of the atoms to form molecules. If the reaction $2H \longrightarrow H_2$ is slow, hydrogen atoms will accumulate and give rise to a greater counter-electromotive force. Different metals may have specific catalytic effects on the rate of this reaction and so give different overvoltages. In practice, one must also take into account the possibility of selective adsorption on the metal of the substance to be reduced. Thus, phenol is hydrogenated at a platinum electrode but practically not at all at a lead cathode, although here the overvoltage is higher.

Another field of study in which Bancroft showed an early interest was that of heterogeneous equilibria, the Cornell Laboratory being the first one in America in which serious work on the practical applications of the phase rule were carried out.

In the Preface to his " Phase Rule." Bancroft classified the facts and phenomena of physical chemistry into the divisions: Qualitative Equilibrium, Quantitative Equilibrium, Electrochemistry, Mathematical Theory. " My idea ", he wrote, " is that all qualitative experimental data should be presented as particular applications of the Phase Rule and the Theorem of Le Chatelier, while the guiding principles for the classification of quantitative phenomena should be the Mass Law and the Theorem of van't Hoff." The view thus expressed explains no doubt why, when Bancroft first began his studies of heterogeneous equilibria with the investigation of ternary mixtures, he approached the subject not from the standpoint of the phase rule but from that of the law of mass action.

The simplest case investigated was that of three liquid components two of which, A and B, are only partially miscible, while the third, S, is miscible in all proportions with A and B separately. Bancroft then considered the amounts of A and B, namely, x and y which will dissolve

simultaneously in a fixed amount of S, and derived the expressions $x^{n_1}y$ = constant and $x^{n_2}y$ = constant, for the two sets of saturated solution. Other expressions were derived for other systems, and these were found to be in harmony with experimental determinations carried out by Bancroft and by his pupils.

Although these early studies of ternary mixtures no longer possess much interest, they no doubt served to direct attention to other ternary liquid systems discussed later in a general manner by Bancroft and investigated experimentally by others according to the principles of the phase rule.

It is worthy of mention that it is to Bancroft that we owe the term " solute," a term which he suggested in his first paper on ternary mixtures presented to the American Academy of Arts and Sciences on May 9th, 1894. While one could be grateful to Bancroft for this useful and generally adopted term, one could not accept his contention that " there is a fundamental difference between the solute and the solvent." One really has some difficulty in understanding how such a view came to be held, for it is not consistent with the definition of a solution, accepted by Bancroft, as a homogeneous mixture the composition of which can undergo continuous variation within limits. This definition neither creates nor recognises any distinction between solvent and solute.

Through drawing a distinction between solvent and solute, Bancroft was led to draw a distinction between fusion curves and solubility curves and so to separate phenomena which are in every respect similar. One must not, however, overemphasise early mistaken views which a growing knowledge and familiarity with the phenomena would soon correct.

To Bancroft we also owe the term " consolute liquids " for liquids which are miscible in all proportions.

At a time when the systematic study of heterogeneous equilibria was still in its early years, Bancroft and his pupils made many valuable contributions to the advancement of knowledge in this domain, a general discussion and exposition of the principles of the phase rule marching hand in hand with the experimental investigation of a wide variety of systems. It is possible to deal here only with some of the most important aspects of Bancroft's work in this field.

Organic chemists had made known the existence of isomeric substances which could exist in two different solid forms, each corresponding to a single definite constitution, but which, in the liquid state, could undergo transformation one into the other until a state of homogeneous equilibrium between the two molecular species was established. The behaviour of such substances gave rise to much controversy, and Bancroft was the first to show that many of the observed facts became more intelligible when one studied the heterogeneous solid–liquid equilibria met with in the case of these " dynamic isomerides." To the value of his work in this domain Ernst Cohen paid tribute in the words: " Einen nicht unwesentlichen Dienst bei dieser Zeit- und Streitfrage auf dem Felde der ' geometrischen ' Isomerie haben auch physikalisch-chemische Untersuchungen geleistet, so namentlich . . . das Studium der Gleichgewichtsverhältnisse von Bancroft."

The behaviour met with in the case of dynamic isomerides depends on the rate of transformation of the one isomer into the other in the liquid state. If the transformation is relatively very rapid, so that equilibrium in the liquid state is rapidly attained, the system will behave like a one-component system; but if the isomeric change is comparatively slow, the behaviour will be that of a two-component system; and, in the absence of compound formation between the isomers, a two-branched freezing-point curve will be obtained.

If isomeric transformation takes place with measurable velocity and if the temperature of the liquid equilibrium mixture is allowed to fall, a point on the freezing-point curve of one of the solid isomers will be reached, and that form will separate out, if supercooling is excluded. This is called the " natural " freezing point. The stable solid modification in the neighbourhood of the melting point is that which is in equilibrium with the liquid phase at the natural freezing point.

The two solid modifications of dynamic isomerides may be monotropic or enantiotropic. It was found by Soch, working in Bancroft's laboratory, that in the neighbourhood of the melting point, the yellow form of benzil-2-carboxylic acid, melting at 141·5°, is the stable form, whereas, at room temperature, the white modification, melting between 125° and 130°, is the stable form. Investigation showed that there is a transition point at about 65°. The two isomeric forms are therefore enantiotropic.

The behaviour of a number of different dynamic isomerides was investigated by Bancroft's pupils.

Bancroft also considered the behaviour of two components which can form a compound.

If the compound is stable, not only in the solid, but also in the liquid state, the equilibrium curve for the compound will consist of two branches meeting at a point, the melting point of the compound. If, however, the compound undergoes dissociation in the liquid state, the dissociation products will lower the freezing point of the compound, and the composition of the liquid will vary continuously with the temperature. The equilibrium curve becomes continuous and the crest of the curve is rounded. The greater the degree of dissociation, the flatter will the curve become, and from the extent of the flattening of the curve one can calculate approximately the degree of dissociation of the compound in the liquid state.

The boiling-point curves of binary liquid mixtures were also investigated by Bancroft and his pupils. Among the mixtures which show a minimum in the boiling-point curve it was found that in many cases one or both of the components is associated. The reason why in such cases a minimum is obtained was first explained by Bancroft as due to the fact that the boiling-point curves of such components intersect.

In other directions, in the investigation of the freezing-point equilibria in three-component systems, in the indirect determination of the composition of the solid phase separating from two-component systems, etc., Bancroft and his pupils were pioneers. At a much later period, when Bancroft's interests had extended to biochemical phenomena, use was made of phase-rule principles in the investigation of the behaviour of proteins towards hydrogen chloride and ammonia. It was shown that casein, zein, arachin, fibrin, and gliadin form no chemical compound with ammonia, and that casein, arachin, fibrin, gliadin, and edestin, but not zein, form definite compounds with hydrogen chloride.

To Bancroft's interest in colloids and the colloid state reference has already been made. In his mind, colloid chemistry, which he defined as " the chemistry of life and inheritance and of bubbles, drops, grains, filaments and films," extended over almost the whole field of chemistry and physical chemistry. The width of its applications, as Bancroft understood it, is indicated by the passage previously quoted from his book " Applied Colloid Chemistry."

Of the subjects which at an early stage attracted Bancroft's interest, one may mention the preparation and properties of emulsions.

In order that a permanent emulsion may be produced on shaking together two immiscible liquids, *e.g.*, water and oil, an emulsifying agent, such as soap, must be added. It is, of course, clear that two different emulsions are possible, an emulsion of oil in water and an emulsion of water in oil. According to the adsorption-film theory of emulsions put forward by Bancroft, an emulsifying agent is adsorbed into the surface separating the two liquids and forms there a coherent film. This film, if in contact with two phases, oil and water, will have two surface tensions, and will tend to curve towards the side having the higher surface tension. The dispersed liquid, therefore, is on the side of the film having the higher surface tension. Since soaps of univalent cations (Na^+,K^+) are readily dispersed in water but not in oil, they form a film which is wetted more readily by water than by oil. Consequently, the surface tension is lower on the water side than on the oil side, and the film tends to curve so that it encloses globules of oil in water. Thereby the area of the side of the film of higher surface tension is reduced compared with that of lower surface tension. Soaps of bivalent cations, however, are freely dispersed in oil, but not in water, and the film is wetted more easily by the oil than by the water. Thereby the formation of globules of water in oil is favoured. According to this theory, the preferential wetting of the adsorbed film by water or by oil is an important factor.

The theory put forward by Bancroft was investigated more fully by his pupils, more especially by G. H. Clowes, and the antagonistic action of Na^+ and Ca^{++} on oil–water emulsions established. This antagonistic action of ions has been found to be of great importance not only in the interpretation of many biological phenomena but also in the oil industry.

In Bancroft's view, surface adsorption was a factor of the greatest importance in many diverse phenomena. In the development of the photographic plate, for example, Bancroft was the first to suggest that adsorption of the developer on the silver bromide grain is the important thing, a view which was later worked out more fully by Sheppard. " If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter, and we shall get a negative. If the reducing agent is adsorbed more strongly to unexposed than to exposed silver bromide, we shall get a positive. If there is not much difference in the adsorptions, we shall have exposed and unexposed silver bromide developing at so nearly the same rate that we get a more or less uniform fogging."

Sensitisers, also, of the photographic plate, Bancroft pointed out, must be such that the dye is adsorbed strongly by the silver bromide, does not bleed into the gelatin sufficiently to act as

a colour screen, and is a reducing agent powerful enough, when exposed to light, to produce a latent image on silver bromide.

In 1922 the First Report, and in the following year the Second Report, of the National Research Council's Committee on Contact Catalysis were published in America. Both reports were written by Bancroft, the chairman of the committee, and were a very stimulating and valuable contribution to the study of contact catalysis. In these reports, which appeared at a time when contact catalysis was largely an empirical art, Bancroft not only showed the position which had been reached but also pointed out what were the fundamental questions which had to be answered and indicated many problems, minor or major, which called for investigation.

For Bancroft, contact catalysis formed an aspect of colloid chemistry and embraced phenomena in which adsorption and surface action play an important part. Two things of fundamental importance, he suggested, had to be done: (1) to determine in what cases definite intermediate compounds are formed, and what they are; (2) to determine what bonds and contravalencies are opened when adsorption takes place and to show that the opening of these bonds and contravalencies accounts for the formation of the reaction products. Later, Bancroft pointed out that the attempt to determine in which group a particular reaction falls, whether there is formation of definite compounds or of indefinite complexes, had led to the brilliant work at Princeton on catalysis at an interface.

In the activation process, however, adsorption is only one factor. "In organic chemistry we get activation and reaction as a result of the formation of radicals . . . The conclusion to be drawn is that the organic chemistry of the future will deal with the reactions of radicals instead of the reactions of the molecules."

Even if it might be difficult to point to direct experimental contributions by Bancroft to the solution of the problems of contact catalysis, there can be no doubt that through his writings he did much to define and clarify the *science* of catalysis and to encourage others to carry out the necessary experimental investigations.

Towards the end of his academic career Bancroft took up the study of anæsthesia, drug addiction, and insanity from the standpoint of colloid chemistry. It can be accepted that for the normal, healthy functioning of the animal organism, a certain balance must be maintained between the degree of dispersion or the hydration and dehydration of the body colloids. Starting with Claude Bernard's theory that the reversible coagulation of the colloids of the sensory nerves produces or accompanies anæsthesia, Bancroft and his co-workers concluded from their experimental investigations that narcotics coagulate reversibly the cell colloids and, conversely, that a reversible coagulation of the cell colloids, however, produced, will cause narcosis. At low concentrations, narcotics may have a stimulating effect by decreasing the stability of the colloids. Similarly, the action of drugs, such as morphine, is due to a coagulation, reversible or irreversible of the nerve colloids. Administration of peptising agents, such as sodium thiocyanate, will facilitate return to normality.

A relation between the state of flocculation or deflocculation of the brain colloids and mental disorders was also believed to have been established, different forms of mental disorder depending on whether the coagulation of the colloids was too great or too little.

The conclusions reached by Bancroft and his fellow-workers led to much controversy and were not entirely confirmed by other research workers. It seems very clear that, although the state of aggregation or dispersion of brain colloids no doubt has a bearing on the physiology of narcosis and insanity, factors of importance other than those considered by Bancroft enter in and affect the colloid state.

On many other problems in colloid chemistry and other sections of physical chemistry, Bancroft shed a powerful light which was both exploratory and clarifying, and the inspiration of his enthusiasm and critical exposition still lives.

For particulars about Bancroft I am indebted more especially to his son-in-law, Professor M. L. Nichols, of Cornell University.

ALEX. FINDLAY.

JOSEPH MICHAEL CONNOLLY.

1913—1952.

Joseph Michael Connolly was born in Loughborough, Leicestershire, on June 3rd, 1913. He was educated at the Loughborough Grammar School (1924—1930) and proceeded to the Loughborough College, where he studied in the Department of Pure and Applied Science, taking the Honours Diploma of that institution and the external honours B.Sc. in chemistry of London University in 1933, both with 2nd Class Honours. During the period 1933—1936 Connolly acted as research assistant to the writer and took his Ph.D. of London externally in 1936. His publications with the writer included several papers in the *Journal* on the chemistry of thiocarbonyl tetrachloride (*J.*, 1934, 822; 1935, 679; 1937, 827).

In 1934 he was appointed as demonstrator in the Department of Pure and Applied Science at Loughborough, and became a full lecturer in 1934, and senior lecturer in 1951. During the latter part of the last decade, however, he became seriously ill with disseminated sclerosis and, although the condition never affected his normally cheerful disposition, both he and his friends knew that the only termination could be a fatal one, and he succumbed to the malady on June 28th, 1952.

Quiet and reserved in nature, Connolly was an excellent chemist, a painstaking teacher and lecturer, and an invaluable member of the department; in private life he was a man of the highest integrity, a pleasant companion, and of that serene disposition which contributed so greatly to his enjoyment of family life. He is survived by his wife and daughter, and will be held in affectionate remembrance by his colleagues and pupils.

G. M. Dyson.

JOSEF LEON HASKELBERG.

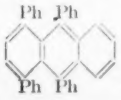
1902—1953.

On January 17th, 1953, death brought to a premature end the scientific career of Dr. Josef Leon Haskelberg, member of the Daniel Sieff Research Institute at Rehovoth, Israel.

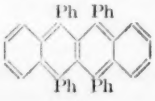
Born on December 28th, 1902, in Warsaw, and educated there, Haskelberg enrolled at the University of Liège in Belgium. Very early in his studies, however, he joined the group of people who were inspired by the idea of a Hebrew University in Jerusalem; he drew the logical conclusion from this idea and emigrated in 1924 to Palestine, where he became one of the first students in the Department of Chemistry at that University and, indeed, one of the pioneers of chemistry in the country. As at that time the Hebrew University did not confer academic degrees, he went in 1928 to Paris to complete his studies at the Sorbonne and receive his degree of D.Sc. In 1933, he returned to Palestine to become (in 1934) one of the Seniors in the Department of Organic Chemistry and Biochemistry at the newly created Daniel Sieff Research Institute.

Haskelberg was an organic chemist in the classical sense of the word. His main interest was in the synthesis of new compounds of possible theoretical and practical interest; he enjoyed the art of synthesis and the preparation of well-defined, beautifully crystallised compounds. In accordance with the general line of work at the Sieff Institute, he specialised in the field of polycyclic aromatic and of potentially chemotherapeutic substances. Amongst the former, the highly phenylated derivatives of the fundamental aromatic hydrocarbons attracted his interest, because of the influence such substitution was bound to exert on their fine structure. Thus, he succeeded in preparing the dark-yellow 1 : 4 : 9 : 10-tetraphenylanthracene (I) which resembled the red rubrene (II) in its autoxidation, its spectrum—which is devoid of all fine structure—and even in its isomerisation under the catalytic influence of acids. Haskelberg's last—unpublished—investigation in this field was directed towards the lower homologue of (I) and (II), 1 : 4 : 5 : 8-tetraphenylnaphthalene (III); the essential step in its synthesis was the diene condensation between the tetraphenylated benz*iso*furan (IV) and maleic anhydride. The hydrocarbon (III), a yellow compound, turned out to be the first photo-oxidisable naphthalene derivative and thus a true homologue of (I) and (II). The obvious deformation of the naphthalene system, caused by the two pairs of phenyl rings, recalls the recent observations by Kloetzel,

Dayton, and Herzog (*J. Amer. Chem. Soc.*, 1950, **72**, 273), Abadir, Cook, and Gibson (*J.*, 1953, 8), and Donaldson and Robertson (*J.*, 1953, 17) on poly*methylated* naphthalenes.



(I)



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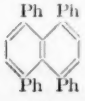

(III)

(IV)

In the chemotherapeutic field, Haskelberg's work was devoted to the preparation of lipophilic derivatives of parent substances, known or likely to exhibit therapeutic activity; it was hoped that these derivatives might be active against the acid-fast bacteria, because of the affinity between the fatty envelope of these bacteria and the lipophilic substituents, and against bacteria which had invaded the lymphatic system of the body. Haskelberg found that introduction of long-chain alkyl or acyl groups, of steroid radicals, and also of highly halogenated side-chains, conferred on many drugs affinity to lipoids; indeed, some of the substances he prepared proved active against tubercle bacilli. These studies were interrupted by the Second World War and were not continued later, as the problems of tuberculosis therapy had in the meantime found other solutions. However, occupation with the synthesis of chemotherapeutic substances enabled Haskelberg during the Second World War to organise, and help in, the production of the complicated drugs which were then in short supply in Palestine, *e.g.*, atebrine and plasmoquine. He thus rendered the country and the Allied armies in the Middle East an invaluable service.

Haskelberg had a strong leaning towards agriculture, and agricultural chemicals became one of his favourite subjects. He studied the synthesis of analogues of DDT and of 2 : 4-D and developed a new method for the preparation of the latter and of similar compounds. In particular, he devoted a great deal of effort to the chemistry of castor oil and the substances derived from it, such as undecenoic acid and heptaldehyde. From the former, he obtained, *e.g.*, by the OXO reaction the 12-oxododecanoic acid which could be converted by reductive amination into 12-aminododecanoic acid. Analogously, he studied the oxidative degradation of undecenoic acid to 10-oxodecanoic and 10-aminodecanoic acid; these amino-acids were expected to afford, on polycondensation, polyamides of the same type as 11-aminoundecanoic acid (Genas, U.S.P. 2,462,855; B.P. 591,027; cf. *Chem. Abs.*, 1948, **42**, 592). Also the chemistry of other unsaturated and, therefore, reactive natural fatty acids was studied in similar directions; it is hoped that the results will be published in the not too distant future.

Haskelberg was passionately fond of nature; he devoted his spare time—as much as the laboratory left him—to gardening, and applied his keen sense of observation to the phenomena of plant life not less than to those of organic chemistry. He was a good colleague, a friend always willing to help, a model citizen interested in every problem of the community, and a patriot of his country; during its War of Independence he served in the Scientific Unit of the Israeli Defence Army. His death is a grievous loss not only to his wife and two daughters, but also to his colleagues, his many friends, and the chemists of Israel.

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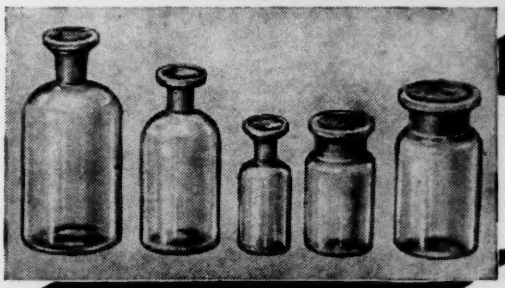

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